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# PROBLEMS OF SPACE BIOLOGY. VOLUME 24. THE WATER SUPPLY OF SPACECRAFT CREWS.

S. V. Chizhov and Yu. Ye. Sinyak

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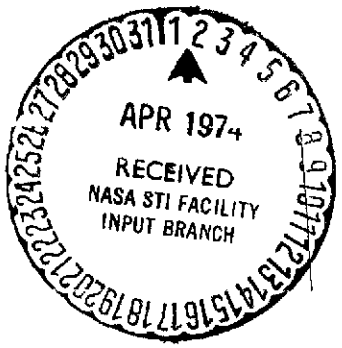


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16. Abstract

Long space voyages will present problems with regard to the water supply to be used by the crew for drinking, washing, cooking, etc. While it may be feasible on shorter trips to simply provide adequate stocks of water for all needs, some form of water recycling or regeneration will be required aboard spacecraft on planetary exploration missions. The book examines various methods of recapturing water from moisture-containing products of human vital activity (feces, urine, sweat) and recycling water used for sanitary and hygienic purposes. Considerable space is devoted to the use of ion-exchange resins and absorbent materials, as well as semipermeable membranes. The problems involved in decontaminating and deodorizing recycled water are examined in detail.

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ANNOTATION

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This book is devoted to one of the most important of medical and technical problems: the water supply of the crews of spacecraft. Questions are discussed which are related to the standards for water consumption, conservation of drinking water, chemical composition of the moisture-containing products of human vital activity and the waste products from biological systems. Considerable attention is devoted to the regeneration of water by means of physical and chemical methods. Methods of desalination and decontamination of regenerated water are discussed. Results of toxicological evaluations of water regenerated by various physical chemical methods are presented. The book is intended for scientific workers, engineers, graduate students and students who are interested in problems involved in the conquest of space.

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## FOREWORD

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In recent years we have seen outstanding successes in the conquest of space. An important role in this achievement has been played by the efficient and reliable functioning of life-support systems, such as the system for purification of the atmosphere to remove harmful impurities, the oxygen supply, and the water supply.

Future space expeditions, aimed at increasing the duration of flights and the numbers of crew members, must include life-support systems that are based on regenerative processes. The water supply system occupies a special place aboard a spacecraft. On long flights, the maximum reduction of liftoff weight can be obtained by organizing recycling of the water.

Development of water supply systems must be preceded by stages of development which involve medical, biological and technological aspects of the problem.

The authors of the present monograph, who have been working in the field of space biotechnology for many years, have conducted extensive studies to develop water supply systems for the crews of spacecraft. The results of these studies are presented for the reader of this book. The book deals with a number of problems associated with the development of water supply systems. An important point in this regard concerns the questions of conservation and decontamination of water as well as toxicological evaluation of water which is obtained by means of a specific regenerative system. Results are presented from studies of various physical and chemical methods of regenerating water from moisture-containing products of human vital activity and waste products from biological-technical systems.

The broad range of methods discussed by the authors will allow planners and designers to select the most desirable solutions for a given spacecraft.

Doctor of Biological Sciences,
Professor A. M. Genin

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# PROBLEMS OF SPACE BIOLOGY.. VOLUME 24. THE WATER SUPPLY OF SPACECRAFT CREWS.

S. V. Chizhov and Yu. Ye. Sinyak

## INTRODUCTION

The development of reliable and effective systems which will ensure the vital activity of the crews of spacecraft, as well as orbital, lunar or planetary stations, constitutes the basis for successful conquest of outer space by man. /7*

Among the basic systems to be found in the cabins of manned spacecraft, a particularly important position is occupied by the systems for regeneration of the atmosphere, water supply and food, with those devices which provide the cosmonaut with water occupying a special place by virtue of the fact that their weight is more than twice as great as the weight of the supplies of oxygen and food products, including samples.

We know that systems that involve carrying water supplies aboard the craft are used for short flights. This calls for reliable methods of storing the water for the planned duration of the flight and developing methods for the storage and decontamination of water supplies with consideration of the use of a number of modern structural materials.

As the length of the flights and the number of crew members increase, the quantity of necessary supplies of oxygen, food and especially water naturally increase as well. Due to the impossibility of increasing the weight of the supplies infinitely, a need arises to find methods of water regeneration aboard the spacecraft, which is one of the central problems in space biotechnology. Its solution will lead to a significant decrease in the weight of the life-support system.

The first publications directed at finding methods of developing water supply systems appeared in the early 1960's. Following the flights of Yu. A. Gagarin on the 12th of April 1961 and G. S. Titov on the 6th of August 1961, more attention was paid to the problem of water supplies for man in flight and consequently there was an increase in the number of published works. During the last ten years, a considerable body of data has been accumulated in many journals from various fields of investigation, thus complicating their use. In this connection, one of the problems dealt with in the present monograph is the systemization and generalization of theoretical and

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*Numbers in the right hand margin indicate pagination in the foreign text.

experimental data on the problem of the water supply of spacecraft crews for the purpose of more successfully using them in the development of planned systems.

The first chapter of the book is devoted to general questions. It deals with problems, as well as approaches to their solution and methods that are associated with the duration of operation of spacecraft.

The second chapter takes up the medical and technical characteristics of /8
the design of water supply systems for spacecraft crews under the conditions that exist on brief flights. Principal emphasis is placed on standards for water supplies and the conservation of drinking water.

In the third chapter, results are presented from studies of the development of water supply systems for long flights. Principal emphasis here is placed on developing physical and chemical methods of water regeneration.

Chapter 4 presents data on studies dealing with the conditioning and decontamination of regenerated water.

Finally, the last chapter discusses methods of medical-biological evaluation of regenerated water and medical checking of the quality of drinking water. Principal emphasis here is placed on the comprehensive hygienic and toxicological evaluation of water which is regenerated from moisture-containing products, as well as methods of decontaminating it.

The authors do not claim that the study of the materials available is complete, and would gratefully accept any critical comments; they hope that the present monograph will be useful to those persons who are interested in the conquest of outer space.

## CHAPTER I: GENERAL PROBLEMS OF THE WATER SUPPLY OF SPACECRAFT CREWS

The importance of water to the human organism is extremely great. Inasmuch as it is a component of all fluids and tissues of the organism, water participates actively in all vital processes. The dipolarity of the water molecule promotes electrolytic dissociation of the salts, acids, alkalis in it, and water is therefore a good solvent for various compounds. Water is a catalyst for many processes in the organism; it is a powerful and at the same time an extremely sensitive thermoregulator, which creates an optimum temperature regime within a very narrow temperature range. /9

We know that water makes up approximately 65% of the total weight of the human organism. The amount of water in vitally important organs is still greater: 79% in heart tissue, 83% in the kidneys, 70% in the liver, 86% in the gray matter of the brain. Despite the considerable amounts of water that participate in vital processes, a lack of it can lead to problems in the vital activity of the organism. Thus, losing only 1% of the water from the total body weight can cause undesirable problems in the functioning of certain organs (Ginetsinskiy, 1964; Greenleaf, 1955). When the water deficit reaches 3-4%, there is a decrease in the working capacity (Kerpel'-Fronius, 1964; Adol'f, 1952; Tursunov, Kravchinskiy, 1963). Loss of 10-20% of the water can have a lethal outcome. Although a man can live more than a month without food, he can only survive a few days without water.

Water deficit in the human organism acquires particular significance when the individual is under spaceflight conditions. The action of accelerations, vibration, weightlessness and tremendous psychological stress lead to increased rates of water excretion from the human organism. It has been found for example that under the influence of hypokinesia and a number of other individual factors that simulate the action of space flight to a certain degree, there is an increased excretion of water and electrolytes by the organism (Natochin, 1965).

As experiments have shown, during the simulation of the effects of certain spaceflight factors on the organism, loss of 3% of the water caused deterioration of the human condition (Balakhovskiy, 1963). In a group of trained individuals, such deterioration was observed only with a 4-5% water deficit. /10
During the flights of the "Mercury" spacecraft the astronauts used comparatively little water. As a result, the total volume of blood in the crew members decreased to the point that, when the spacecraft splashed down and their weight was restored, the astronauts were in a semi-fainting condition.

All of the above indicate the need for developing systems that will provide cosmonauts with an adequate supply of potable water under appropriate conditions for its consumption.

## Life-Support Systems Based on Supplies and Recycling of Materials

The water supply system for spacecraft crews constitutes a portion of the general system for supporting vital activity of man in flight. The latter, since it consists of a combination of many links, may be structured in various ways depending on the duration of the spaceflight. However, a common feature of all types of systems is a satisfaction of the physiological needs of man for oxygen, water and food.

Theoretically, there are two possible approaches to designing systems for ensuring the vital activity of man in flight:

a) establishing of supplies of oxygen, water and food;

b) use of regeneration processes to obtain them.

Obviously, under actual conditions it is difficult to draw a clear line between these two approaches. In all likelihood, it will be necessary first of all to use systems that are based exclusively on supplies and then later, as the duration of the flights increase, individual regeneration processes will be switched to take over the production of certain components and it is only after this that we can speak of a partial or complete recycling of materials.

Systems that are based on supplies are characterized by a high reliability, extremely low energy consumption and considerable convenience in operation. However, they are only effective for short flights or on long expeditions when a necessary prerequisite will be a regular replacement of supplies by means of shuttle craft.

The difficulty with life-support systems based on supplies follows from the weight characteristics of oxygen, water and food, the daily standards for whose consumption as calculated for one man (in kg) are presented below (Bykov, 1959; Krotkov, 1959; Zbarskiy, Bambeneck, 1959; Hawkins, 1958):

| | |
|---|---|
| Oxygen | 1 |
| Water | 4 |
| Food | 0.5-0.7 |
| fats | 0.1 |
| proteins | 0.1 |
| carbohydrates | 0.4 |
| salts | 0.02 |

As we can see, the daily amounts of all vitally important products, /11
without taking into account the weight of the containers for storing them, can reach 6 kg per man. It must be pointed out in this context that the weight of the water supply is nearly twice the combined weight of the oxygen and food supplies taken together.

Hence, under conditions of short flights the supplies are still relatively small and consist, for example in the case of a 24-hour or 7-day flight by a

3-man crew, of 16-17 and 115-120 kg, respectively. Increasing the number of crew members or the duration of operation of the spacecraft causes the weight (and the dimensions of the system) to increase to the point where using them becomes very difficult (Table 1) (Sinyak, Chizhov, 1964).

TABLE 1.* WEIGHT (in kg) OF OXYGEN, WATER AND FOOD FOR ONE- AND THREE-MAN CREWS AS A FUNCTION OF FLIGHT DURATION

| Flight duration, days | One man | | | | Three men | | | |
|---|---|---|---|---|---|---|---|---|
| | Oxygen | Water | Food (dry) | Total weight | Oxygen | Water | Food (dry) | Total weight |
| 1 | 1 | 4 | 0,5 | 5,5 | 3 | 12 | 1,5 | 16,5 |
| 7 | 7 | 28 | 3,5 | 38,5 | 21 | 84 | 10,5 | 115,5 |
| 30 | 30 | 120 | 15 | 165 | 90 | 360 | 45 | 495 |
| 182 | 182 | 728 | 91 | 1 001 | 546 | 2 184 | 273 | 3 003 |
| 365 | 365 | 1460 | 182,5 | 2 007 | 1095 | 4 380 | 547,5 | 6 022 |
| 730 | 730 | 2920 | 365 | 4 015 | 2190 | 8 760 | 1095 | 12 044 |
| 1820 | 1820 | 7300 | 912 | 10 037 | 4675 | 22 900 | 2737 | 30 112 |

*Note: Commas indicate decimal points.

It is clear from the table that the weight of the oxygen, water and food supplies for a 3-man crew on a 3-year flight (the rough figure for a trip from Earth to Mars and back to Earth) would be more than 30,000 kg. This value increases considerably if we take into account the weight of the containers and the equipment necessary for storing these products, especially gaseous oxygen. In addition to the increased weight and size parameters associated with these supply-based systems, the latter cannot solve those problems that are related to the storage or elimination of the waste products of human vital activity, whose weight may be equal to the weight of the stored oxygen, water and food.

Hence, the high weight of the supply-based systems as well as the complexity of the problems associated with the prolonged storage of oxygen, food and the waste products of human vital activity necessitate the use of regeneration processes for creating the means of life support aboard spacecraft.

General Recycling of Materials in Closed Systems and the Water Supply Branch

In all probability, the most promising system for ensuring vital activity /12 is a system which is based on the principle of recycling of materials. The maintenance of human vital activity is not accomplished through the irreversible absorption of chemical elements but as a result of the utilization of energy in complex chemical and biochemical compounds (Shepalev, 1963).

The chemical elements of compounds that are unsuited for further utilization, transformed by means of various methods (for example photo- or chemosynthesis), may be used in processes of synthesis and catalysis that are

repeated many times over. Theoretically, it is not necessary to have supplies of material aboard the spacecraft to ensure functioning of such a system. The raw materials for developing a continuous recycling of materials may be the solid and fluid wastes from man and animals, products of vital excretion of algae and plants, as well as the inedible parts of plants and animals.

Under terrestrial conditions, recycling of material constitutes a tremendous complex of links and processes. All of the links are interrelated so that each successive link uses the products of the activity of one or more preceding ones. The periods of cycling of elements under these conditions are extremely long and amount (for example, in the case of oxygen and nitrogen) to about $5 \cdot 10^3$ and $10^8$ years (Vernadskiy, 1956).

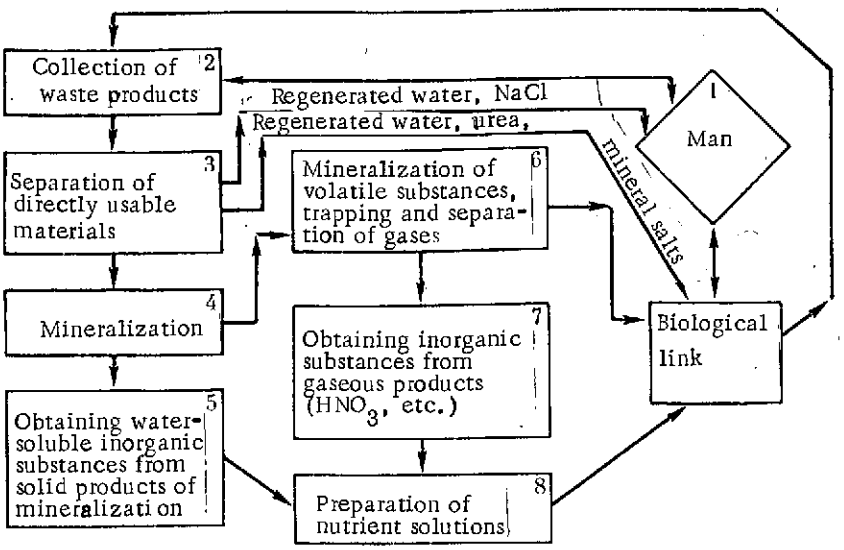
Aboard a spacecraft, a system which is based on the recycling of materials, due to weight limitations, cannot consist of a great many different links. Therefore, it is necessary to have one link that includes a limited number of processes which will ensure stable functioning of the system with the shortest time cycle. Such a link must be the utilization link, whose purpose is to process the products of human vital activity and the waste products from the biological components into a form which is suitable for further utilization by them. The utilization link may be based on either biological or physical-chemical processes, or a combination of the two.

We know that microorganisms cause the breakdown of organic compounds to form carbon dioxide, nitrate salts and so on, which can be absorbed by plants (Ruban, 1961; Kuznetsov, 1962). This breakdown proceeds most intensively under conditions of aerobic conduct of the process. A promising method for biological recycling of waste products under spaceflight conditions is utilization involving participation of photosynthetic algae (Vinberg, 1960).

The principal advantage of the biological method of utilization consists in the need for only small energy consumption. However, the use of microorganisms under actual flight conditions poses certain difficulties. Thus, using microbiological mineralization, it is very difficult to achieve total oxidation of organic compounds (for example, cellulose). The technology of the process requires considerable dilution of the waste products by water (Tsitovich, 1966), leading to an increase in the weight and size of the system. In addition, mutations are possible under the influence of radiation or other specific flight conditions. /13

Physical and chemical processes are free of the shortcomings of biological methods since they are characterized by total reprocessing and high speed, as well as the possibility of automation and control.

One possible arrangement for the utilization link employing physical and chemical processes is shown below:




The products of human vital activity (1) and the waste products from the biological link (9) are placed in a collector (2). In unit (3) the water, sodium chloride and other compounds which can be used directly by man or plants are separated. The remaining material is subjected to mineralization (oxidation) in the appropriate section (4). Section (5) is used for conversion of solid materials, formed as the result of mineralization, into soluble compounds (salts). Dissolution may be accomplished by means of acids that are formed from gaseous oxides of sulfur or nitrogen in sections (6) and (7). The nutrient solutions prepared in section (8) enter the biological link for growing plants.

This sequence of conversions is only one possible variation of the system for physical and chemical transformation of substances in a spacecraft cabin. /14
One of the main sections for utilization of waste products is their mineralization or oxidation. Generally speaking, mineralization is an "unprofitable" process from the energy standpoint, inasmuch as the energy from the organic compounds of the products of vital activity are liberated in the form of heat, which it is very difficult to utilize. Nevertheless, mineralization makes it possible to change a remarkably broad range of chemical compounds of waste products to a limited number of oxides for subsequent utilization in the preparation of nutrient solutions for the cultivation of lower and higher plants.

One of the most widely investigated methods of mineralization is thermal combustion. At 950° and atmospheric pressure it is possible to oxidize the organic components of feces to form ash and a mixture of gaseous products that consist of $CO_2$, $O_2$, $H_2O$ and several other compounds (Balin et al., 1967). The mineralization temperature can be reduced by using the method of "moist combustion."

Using a pressure of 150 atmospheres and a temperature of 200-300°, we achieved 90-95% mineralization of products of human vital activity (Drigo, 1967). The resultant solution contained mineral salts, ammonia and many elements which make it possible to use it for growing plants.

The shortcomings of these methods (high temperatures in the case of thermal mineralization and increased pressures that are associated with "moist" combustion) can be eliminated if the oxidation process is conducted in the presence of catalysts. The oxidation-catalytic method is characterized by comparatively mild conditions (atmospheric pressure, temperature 300-400°) and makes it possible to mineralize all of the products of human vital activity and waste products from biological systems (Sinyak, Uspenskaya, 1965; Kuznetsov, Sinyak, Shul'gina, 1966).

To dissolve the ash and prepare the nutrient solutions, we can use the catalytic method of obtaining ammonia water and nitric acid from the urea in human urine (Belyakova, Sinyak, 1967).

Cultivating plants with nutrient solutions results in an accumulation of sodium chloride, which leads to undesirable consequences. Therefore, methods have been developed for separating the NaCl both to prevent salination of the culture medium and to obtain table salt for the cosmonauts to use. The problem of trapping and separating gases and making acids from them may be solved by using catalytic, chromatographic and sorptive methods.

The data which we have examined indicate that there is a possibility of developing a utilization link which is based on physical and chemical methods. It should be pointed out that these physical and chemical methods and processes require a certain amount of energy for their realization, which naturally decreases their value somewhat. However, the use of isotope heat /15
sources or small nuclear reactors will make it possible to solve these problems.

An outstanding feature of the physical and chemical methods is not only their suitability for developing the utilization link but also the possibility of using them to produce high-energy chemical compounds (fats, amino acids, carbohydrates), required for human consumption. Thus, on the basis of work by A. M. Butlerov (1861), Kuzin (1940), Balezin (1947) and others, the possibility of obtaining carbohydrates and monosaccharides from the products of human vital activity was demonstrated theoretically and experimentally (Akerlof, 1964; Sinyak, 1964, 1968; Sinyak, Uspenskaya, 1965, 1967; Shapira, 1963; Ugolev et al., 1969; Berlin, Krylov, Sinyak, 1970; Krylov et al., 1970, 1971; Uspenskaya, Krylov, Sinyak, 1971).

In view of the complexity associated with developing life-support systems for use aboard spacecraft in which there is a total recycling of substances, we feel that the most rational approach would be a gradual introduction of autonomous cycling of individual substances in supply-based systems. A particular case of the total recycling of materials is the recycling of water. Development of a system that would make it possible to achieve multiple

utilization of water regenerated in the craft itself would make it possible to reduce considerably the liftoff weight of spacecraft.

The problem of developing recycling of water is also being solved in stages, by the method of successive approximation. On short flights, due to the low energy supplies aboard the craft, it is advantageous to incorporate regeneration processes for purification of slightly concentrated waste products. Consequently, systems will be developed in the future for regeneration of water from more polluted solutions; finally total water recycling will be accomplished on long expeditions.

## CHAPTER II: WATER SUPPLY SYSTEMS BASED ON SUPPLIES

The development of water supply systems for the crews of spacecraft under the conditions of short flights is closely linked to the development of standards of water consumption and the problem of conservation of drinking water with its properties unchanged through preservation. /16

The determination of the exact amount of water required by a cosmonaut makes it possible on the one hand to avoid "straining" the system, allowing minimization of the weight of the water not used during the flight; one the other hand, it makes it possible to avoid the danger of a water shortage and the resultant disturbances to the vital activity of the organism.

The choice of effective preservatives for water which are harmless to man and retain high physical-chemical and organoleptic levels of quality makes it possible to ensure a high level of working capacity for the cosmonaut under the difficult conditions of space flight.

### Standards for Water Consumption for the Crews of Spacecraft

The basis for the precise standard for water consumption for an individual crew member aboard a spacecraft is a problem which is difficult to solve. The level of daily water consumption will be affected by the individual characteristics of the cosmonauts, the food ration, the nature and degree of physical stress, morale effects, temperature, humidity, barometric pressure and the composition of the atmosphere of the craft. In addition, the standard for water consumption also depends on such factors as g-forces, weightlessness, isolation, vibration, and so forth. It should be pointed out that some of these factors will promote an increase in the level of water consumption (for example, increased temperature, reduced atmospheric pressure, wearing of a space suit); others will cause a reduction in water consumption (hypokinesia and several others). Even in the case of an individual who is on Earth in comfortable circumstances, the daily standard of water consumption can vary within wide limits. Thus, S. M. Cherkinskiy (1962) recommends a standard of two liters a day for a man who is at moderate temperature and is working for an average period of time. Kerpel'-Fronius (1964) and Kravchinskiy (1963) conclude that an individual will use from 2.5 to 3 liters of water each day. /17 According to the data of N. V. Dolgov, the daily consumption of water by man is 2.5-3.5 liters.

A number of researchers, on the basis of the standards of water consumption by man, have suggested that the energy losses and energy levels of the food ration should be taken into account. Thus, Kerpel'-Fronius (1964) and Lowrey and Roy (1963) feel that an individual must take in 1 ml of water for each calorie of food. In the opinion of Jackson (1968), the figure of 1 ml of water per kcal of food should be increased. Increasing the ambient temperature and the intensity of physical stress causes an abrupt rise in water consumption by the organism. In these cases the standard for water consumption could reach 5 liters or more (Cherkinskiy, 1962). Under desert conditions, it is recommended that up to 6-11 liters of water be used each day (Adol'f, 1952; Dill, 1938).

F. G. Krotkov (1958) recommends a daily water consumption level of 2.5 to 3.5 liters for soldiers performing work characteristic of the military profession at high air temperatures. It is obvious that this standard is worthy of special attention, since the author has selected conditions that are quite similar to those experienced by an individual in a closed, hermetically sealed chamber.

This data on the water needs of man indicate that there is a considerable variation in the latter. Obviously, we must use as the basis for the scientific establishment of standards for water consumption the principle of maintenance of water balance between man and the environment. In other words, the actual standard for the consumption of water will be the amount which corresponds to the quantity of fluid lost by the organism in a specified time interval, taking into account the metabolic water which is formed as a result of oxidation of substances that go to make up the food ration. Therefore, considerable importance attaches to the determination of the relationship of the amount of moisture given off by the organism to various spaceflight factors.

Excretion of water by man takes place in the following principal ways: through the kidneys, skin, respiratory organs and gastrointestinal tract. Under comfortable environmental conditions and mild physical exercise, the water lost in these ways by the organism is in the ratio of 6:2:2:1 (Danelov, 1956). However, this ratio can change widely when the individual is under specific conditions.

Under normal physical conditions, one of the main organs of the excretory system which changes the excretion of water and salt as a function of the needs of the organism is the kidney. Thanks to this characteristic, the kidney is able to maintain a constant internal environment in the organism which adequately copes with conditions. In the complex chain of reflexes which regulate the homeostasis of the fluids of the organism, the kidney is the principal effector organ. In the norm, the kidneys carry out many different functions, which can be conditionally divided into two large groups:

- maintenance of the internal environment of the organism at a constant level; /18
- excretion of the products of metabolism and toxic compounds that are formed in the course of metabolism.

This activity of the kidneys is linked to their primary function -- the formation of urine and its excretion.

At the present time, the formation of urine is viewed as a filtration-reabsorption-secretion process which can be described as follows. The first stage in the formation of urine is the process of glomerular filtration of the blood plasma, which passes through the capillaries of the glomerulus. Filtration is caused by the difference between the hydrostatic pressure in the capillaries and the colloidosmotic pressure in the plasma. The fluid which enters the Bowman's capsule is identical in chemical composition to the plasma but lacks proteins. The protein-free plasma ultrafiltrate which is formed in

the glomeruli, on traveling further through the kidney tubules, undergoes changes due to processes of reabsorption, secretion, and the synthesis of a number of substances, and is converted into the final product -- the urine in the bladder, which differs considerably in composition from the plasma (Kravchinskiy, 1958; Vovsi, 1960; Zaretskiy, 1963; Pandov, 1965).

Water enters the lumen of the kidney tubules through the glomerulus, whose membrane is not impermeable to it. Of the 150-180 liters of primary urine which passes through the kidneys each day, only 1-1.5 liters is excreted in the form of definitive (final) urine. However, the overwhelming majority of the water (about 99%) is reabsorbed in the tubules. The absorption of the water in the various parts of the kidney tubules takes place differently. The proximal tubules are highly permeable to water. They carry out an obligatory passive absorption of it. The water moves passively to and fro in the proximal tubule, according to the laws of osmosis and diffusion, following the movements of the dissolved substances. Here, seven-eighths of the total glomerular filtrate is reabsorbed. Throughout the entire length of the proximal tubules, the fluid is isotonic with respect to plasma.

The descending portion of the loop of Henle is permeable to water, so that the urine becomes concentrated and hypertonic. Near the bend in the loop, the osmolarity reaches its maximum. The ascending branch of the loop of Henle and the beginning of the long canaliculus are practically impermeable to water, leading to a decrease in the osmolarity, inasmuch as the sodium is reabsorbed and hypertonic urine enters the initial section of the distal tubule. The permeability of the distal tubule to water as well as that of the collecting duct is under the control of anti-diuretic hormone (ADH). In the normal individual, 12-15% of the total amount of water that enters will be absorbed in this part of the nephron. Reabsorption of water is subject to quantitative variations here and is referred to as facultative. It is precisely because of these variations that the kidney can excrete urine with a greater or lesser concentration in comparison with the plasma.

According to the data of V. S. Gulevich (1967), B. D. Kravchinskiy (1963), /19
N. V. Danilov (1956), N. N. Pushkina, (1963), N. B. Zbarskiy, P. I. Ivanova (1960), S. R. Mardashov, P. Georgescu, Peunescu (1963), Ionov (1965), E. Adol'f (1952), E. Kerpel'-Fronius (1964), F. B. Shtraub (1965), and others, the daily diuresis in man is 1,200 to 1,500 ml. In exceptional cases, the amount of urine excreted per day can reach 8-12 liters (Kravchinskiy, 1963; Kerpel'-Fronius, 1964). When water consumption is limited, diuresis may fall to 0.5 liter per day (Gamble, 1951; Danilov, 1956). It is considered that this is the minimal level of diuresis which makes it possible to extract all of the products of metabolism that are formed in the organism. This diuresis may occur as a result of a sharp limitation in the intake of fluid into the organism or during increased sweating (Ginetsinskiy, 1962).

The following are data from various authors on the daily level of diuresis in man (in ml):

| | |
|---|---|
| Gulevich (1945) | 1,100-1,600 |
| Pushkina (1963) | 1,200-1,500 |
| Ferdman (1962) | 1,500 |
| Tolkachevskaya (1940) | 900-1,500 |
| Danilov (1956) | 1,200-1,500 |
| Ginetsinskiy (1963) | 1,500 |
| Proctor (1963) | 1,300 |
| Rudek (1965) | 1,215 |
| Bambenek (1959) | 1,200 |
| Hendel (1964) | 1,200 |
| Zbarskiy (1960) | 1,200-1,500 |

As we can see, the daily diuresis in man varies within rather wide limits and is a function of a number of factors which we discussed earlier.

Popov (1966) and Belykh (1958) feel that excretion of water and other dense components of the urine varies as a function of the daily working rhythm of the kidneys. In a healthy individual the diurnal diuresis exceeds the nocturnal by a proportion of 4:1 or 3:1. At night, between 0300 and 0600, the smallest amount of urine is excreted; most of the urine is excreted between 1400 and 1800. In these portions of urine, the lowest concentration of solid components will be found. It must be taken into account that this cyclic nature of the daily excretion of urine is nearly independent of the time that the water and food were taken into the organism. The above facts must also be taken into account when developing a work schedule for the regeneration systems that will recover water from urine.

However, we are particularly interested in studies in which data are presented on the levels of daily diuresis in man when the latter is exposed to conditions similar in certain respects to spaceflight conditions.

The majority of researchers who have studied diuresis in man when the latter is in a hermetically sealed environment note a tendency toward a decrease under these conditions. For example, Yu. G. Nefedov, V. V. Zhuravelev and others (1963-1965), studying man in hermetically sealed chambers, have found that in the course of a 15-day experiment the daily excretion of urine was 1,040 ml, in a 30-day experiment, 1,036-1,445 ml and in a 125-day experiment, 1,117 ml. In similar experiments, Celentano (1963) found the daily excretion of urine to be 850-1,130 ml. /20

As a result of studies of diuresis that were conducted on cosmonauts and astronauts during the flights of the "Voskhod" and "Gemini", on the other hand, an increase in urine secretion was observed in man during space flights. Thus, according to the data from Soviet authors I. S. Balakhovskiy, L. F. Vasil'yev, Yu. V. Natochin, A. I. Grigor'yev and others (1965-1966), and G. I. Kozyrevskaya (1970), there is a pronounced regularity in the increase in the water-excretory function of the kidneys under the influence of spaceflight factors in the organism. This position was also taken in a number of articles by American researchers. Thus, Graveline (1964) writes, for example, that despite the considerable limitation of information during the first and second manned space flights in the United States, an increase in the amount of

urine was noted, with a low specific gravity (up to 1003). The author feels that the dilution of the urine indicated its increased excretion from the organism of the cosmonaut. Berry (1969) also emphasizes that in analyzing the results of medical and biological studies that were performed under actual spaceflight conditions, one is struck by the increase in diuresis with decreasing specific gravity of the urine. The reason for polyuria during weightlessness, in the opinion of the majority of researchers, is the decrease in the production of ADH and aldosterone as a result of the hyperemia of the organs of the chest when the hydrostatic pressure of the column of blood decreases (the Henry-Gauer reflex).

Immediately after landing, according to data from the majority of researchers (Natochin et al., 1965; Grigor'yev, 1970; Balakhovskiy et al., 1971; Berry et al., 1962, 1966, etc.), the amount of fluid excreted by the kidneys decreases markedly. In testing a 2% water load, it was found that there was a drop in the amount of excreted urine as indicated by a number of factors. This is a result of a reinforcement of the osmoregulatory systems for the purpose of restoring the adequate fluid level in the organism. In studying the results of medical examinations in the "Gemini", "Vostok", "Voskhod" and "Soyuz" programs, the researchers noted that 24-48 hours after the space flight the diuresis of the cosmonauts increased and reached its normal level.

A number of Soviet and foreign researchers have concluded that when an individual remains in a closed environment there is a tendency toward decreased diuresis and increased water excretion with the perspiration and expired air. However, it is advisable to study these data in greater detail when we examine papers devoted to a study of water balance in man when the latter has been in a closed environment.

The second way in which a significant amount of fluid is lost from the human organism is through the skin and lungs. At the present time, imperceptible perspiration is viewed as a physical process involving the passage of water in the form of vapor through the epidermis (Kuno, 1961, etc.). A great many studies have shown that the intensity of the imperceptible perspiration increases as the barometric pressure falls, when the skin temperature increases, and after intake of food and physical exercise (Korngeym, 1934; Shatalina, 1964; Kuno, 1961; Vakkar, Chernykov, 1966, etc.). Under comfortable conditions, the level of skin perspiration is 16 grams per hour from 1 $m^2$ of surface. The ratio between the cutaneous and respiratory perspiration is a function of the humidity of the inspired air. Thus, at normal air humidity the ratio is 1:2:7; when it is very humid, it is 1:3:3 and when it is very dry -- 1:2, (Kuno, 1961). On the average, the total value of imperceptible perspiration is 23 ml per hour per 1 $m^2$ of surface. The obligatory daily losses of moisture include perspiration from the palms, soles of the feet and armpits. Despite the fact that the total surface of these areas is less than 10% of the total body surface, the level of constant perspiration is sufficient and is a component of the total level of daily imperceptible perspiration. /21

Perspiration and water vapor in the expired air, at comfortable temperatures while performing light work, amounts to about 1 liter of fluid per day which is condensed by the air-conditioning system of the spacecraft cabin.

However, the amount of fluid lost through the skin and lungs varies within significant limits and is a function of the thermoregulation of the organism and a number of other factors. Active excretion of perspiration can occur in response to an increase in the temperature of the environment, physical work, mental and emotional stress and so forth. Despite the fact that the total surface of the sweat glands is 60-90 $cm^2$, the amount of perspiration given off in response to a given stimulus can reach 10 liters a day. Particular attention should be given to perspiration under conditions of high ambient temperature and increased physical stress. While a need for increased thermoregulation of the organism arises under these conditions, the degree of its dehydration may be intensified, since perspiration takes place with a water deficit (Adol'f, 1952; Kuno, 1961; Ginetsinskiy, 1963, and others).

Changes in water-salt balance can occur in the event of a disturbance of the function of the gastro-intestinal tract (vomiting, diarrhea). Thus, according to the data of Kerpel'-Fronius (1964), in the course of 24 hours about 8 liters of various secretions enter the gastro-intestinal tract; the following are expressed in ml:

| | |
|---|---|
| Saliva | 1,500 |
| Gastric juice | 2,500 |
| Bile | 400 |
| Pancreatic juice | 600 |
| Intestinal juice | 3,000 |
| Total | 8,000 |

Cessation of absorption of digestive juices would lead to a loss of nearly half of the extracellular fluid within 24 hours, but since the secretions given off by the glands contain many salts, the result would be not only dehydration but salt deficit (Kerpel'-Fronius, 1964; Chudnovskiy, 1966; Vasil'tishchev, 1967 and others). Similar troubles may arise both under the influence of the specific stimuli of gastro-intestinal ailments and in response to stimulation of the cortical and vegetative centers, and under conditions of severe emotional stress. /22

Hence, these factors cause the development of a number of response reactions on the part of the organism which result in losses of water and salts. The question of standardizing the water with consideration of these data which characterize the routes and amounts by and in which it is excreted from the organism would appear at first glance to pose no particular difficulty. However, the mere fact that the recommended standards for water consumption for man, even under ordinary terrestrial conditions, vary within such significant limits indicates the complexity of the problem at hand and the limited extent to which these standards have been developed, especially for spaceflight conditions. There are many papers in which the authors use calculations (without experimental verification) to recommend certain standards for water consumption for cosmonauts under spaceflight conditions.

The statements of these researchers are of dual interest. On the one hand, on the basis of these data, it is necessary to calculate correctly the

necessary water supply for each crew member for the entire duration of the flight. On the other hand, when using a water-regeneration system, it is necessary to calculate the daily cycle and work schedule for the regeneration apparatus.

Let us discuss some of the papers in which recommendations are given for water-consumption standards for flight conditions on the basis of calculated data. Thus, Bambenek (1959) points out in his publications that under spaceflight conditions the daily drinking water needs of a man weighing 70 to 75 kg would be 2.0-2.5 liters. Later, this view was supported by other researchers (Briggs, 1962; Purie, 1965; Matter, 1960; Rudek, 1967; Canin, 1962; Chizhov, 1964).

In 1960, Still, in describing the American spacecraft intended for flights to the Moon, emphasized that normal vital activity under these conditions would be ensured by having a daily water consumption of 2.13 kg. However, the author points out that if the flight conditions should change, this standard for water consumption would change as well. Whisenhunt (1961), in devising standards for water consumption for the 3-man crew aboard the spacecraft laboratory known as the "Satellab", suggests that each man would use 2,095 ml of water each day. This standard includes the water in food (225 ml) and the water used for drinking (1,870 ml). He points out that this standard would have to be checked carefully if lyophilized products are included in the diet. /23 The author points out, however, that water consumption may change considerably as a function of the activity of the crew members and the ambient temperature. In addition, another group of researchers (Macklin, 1964; Hendel, Frank, 1962; Smylie, 1964; Hansen, 1965) feel that the standard for daily water consumption for cosmonauts must be higher, from 2,500 to 3,000 ml. As a result of this analysis of the basic works, whose authors propose various standards for water consumption, it follows that these standards vary within rather broad limits and depend upon a number of factors. In addition to the ambient temperature, the intensity of physical stress, the type of clothing and the composition of the diet, the level of water balance is also affected by spaceflight factors (g-forces, weightlessness, acceleration and so on), although these problems have not yet been adequately studied. Mention should be made of the work of Yu. V. Natochin et al. (1965), A. I. Grigor'yev, G. I. Kozyrevskaya (1970); I. S. Balakhovsky, et al. (1966-1971); Berry, et al. (1967) and Fischer, et al. (1967) in which specific reactions and variations involving water-salt metabolism in cosmonauts during flight and during the examination were mentioned. It follows from these studies that phenomena of dehydration occur in the human organism under the influence of spaceflight factors so that the amount of water which is required by the cosmonaut may increase.

It has been known for a long time that hypohydration may result in serious physiological problems in the organism. However, the data in the literature on the magnitude of the water deficit producing functional disturbances in the organisms, do not agree. Many authors (Ladell, 1955; Greenleaf et al., 1966) even consider a water loss of 2-3% useful when carrying out tasks associated with stressful effects.[1] In their opinion, a fluid loss of up to 4% will not

[1]Here and in the following, the percentage of fluid loss will be given relative to body weight.

produce significant physiological disturbances in the organism if the decrease in renal activity is not taken into account. In contrast to this point of view, some feel that any (even an insignificant) water deficit is harmful to the organism (Buskirk, Deedham, 1960; Saltin, 1964). According to the data of Adol'f (1952), when the organism is dehydrated by 3-4% (under conditions of a harsh climate and in ordinary schedule of activity) there is a decrease in muscle tone and motor activity.

Soviet researchers (Ginetsinsky, 1963; Kravchinsky, 1963) feel that hypohydration by 1-2% can cause significant problems with the vital activity of the organism, while a loss of 5-6% of the body weight due to fluid loss causes a decline in mental and physical working capacity, rapid fatigue and weakness. With 15-20% hypohydration, death ensues. Similar data are presented by Marrift (1950) but he suggests that with a 6% water deficit (a moderate degree /24
of hypohydration according to his classification) working capacity is still retained but considerably reduced, and is lost only with a severe degree of dehydration (7-14%).

Specialists in space medicine have confirmed that with a dehydration of more than 3-4% there is a decrease in orthostatic stability (Vanyusha et al., 1966) and tolerance to g-forces, (Taliaferro et al, 1965; Greenleaf et al., 1966), a sharp decrease in working time with maximum stress (Saltin, 1964). In their opinion, hypohydration of more than 4% is "serious physiological stress", especially if it develops rapidly.

Hence, in the opinion of a majority of researchers, dehydration of more than 3-4% is not safe for human life. From data from medical examinations during postflight periods, we know that the Soviet and the American cosmonauts and astronauts lost from 2-6% of their initial weight during orbital flights (Balakhovskiy, 1966-1971; Vorob'yev et al., 1967; Grigor'yev, Kozyravskaya, 1970; Berry, Catterson, 1967; Fischer et al., 1967; Webb, 1967 and others). An analysis of the results has shown that weight loss is not a function of flight time. Following the landing, the cosmonauts practically regained their preflight weight in two days. This enabled the authors to suggest that the decrease in body weight during a flight lasting up to 5 days is caused mainly by fluid losses.

A considerable influence on the nature of renal excretion of fluids is exerted by g-forces. Under the influence of transverse accelerations, Stauffer (1951), Mechan (1961), Bricker et al., 1967) and other researchers, observed oliguria. Similar results were observed under positive g-forces (Rogge et al., 1967; Bricker et al., 1967), the authors explain the data they obtained by attributing it to an increase in ADH secretion. Following exposure to accelerations, Vasil'yev et al., (1967), Slonim (1961), Watson, Rapp (1962; Korotayev, Grigor'yev, (1967); and Kozyrevskaya, Grigor'yev and Koloskova (1970) observed an increase in the quantity of excreted urine which, in the opinion of the majority of researchers, involved an increase in the rate of glomerular filtration and a decrease in ADH production.

One of the spaceflight factors which affect water balance in man is the limitation of the mobility of the individual. In order to determine the

significance of this factor, Kozyrevskaya et al., (1970) studied the changes in water-salt metabolism under conditions of 62-day hypokinesia. The author studied water-salt metabolism in two groups of subjects (3 individuals each) kept for 62 days under conditions of strict bedrest. The first group of subjects was kept under conditions of limited motor activity while the second group carried out a special program of physical exercises each day without getting out of the horizontal position. The results of the study of the dynamics of water consumption and diuresis showed that both groups, by the end of the experiment, showed a decrease in water consumption, while there was an increase in diuresis by the 4th to 6th week. The following are the data on water consumption (in ml/kg) for the entire experiment: /25

| Time, Weeks | First Group | Second Group |
|---|---|---|
| 1 | 35.8 | 36.2 |
| 3 | 35.2 | 35.0 |
| 5 | 30.0 | 31.0 |
| 8 | 22.0 | 24.0 |

Studies of calcium metabolism have shown that it increases in the blood, urine and feces, while there is a decrease in the optical density of bone tissue in x-rays (Biryukov et al., 1967). The group of subjects who performed the physical exercises showed less severe decalcification. However, on the whole, the physical stress had no influence on the pattern of water-salt metabolism. The authors concluded that the principal factor which governs the dynamics of water metabolism is the decrease in hydrostatic pressure of the column of blood in the large vessels, caused by the horizontal position of the body. These results acquire very important significance in weightless conditions when the hydrostatic pressure gradient vanishes completely.

Clammann (1961), who studied water-salt metabolism in a man when the latter was kept in a state of isolation in a hermetically sealed cabin at atmospheric pressure, found the daily standard for water consumption to be 2,200 ml:

| Consumption, grams | | Excretion, grams | |
|---|---|---|---|
| Water | 2,200 | Urine, perspiration and sweating | 2,542 |
| Food | 523 | Metabolic water | 342 |
| Oxygen | 862 | Carbon dioxide | 982 |

From these it follows that the quantity of excreted fluid exceeds the consumption of water by 342 grams. This is the so-called metabolic water which is formed in the organism by oxidative processes.

Considerable interest attaches to the work of Morgan (1962), who presented the results of observations of water balance in two subjects who were kept in a spacecraft simulator cabin. Following the end of a 17-day experiment which was conducted at $t = 23^{\circ}$, a relative humidity of 50-70% and reduced pressure, the subject showed body weight losses with simultaneous decrease of

the plasma volume in the organism. The authors state that the principal cause of dehydration was decreased extracellular water, despite normal water supplies. To establish the standards for water consumption, the authors of this monograph performed a series of experiments whose conditions were as close as possible to actual spaceflight conditions. Two subjects were placed in a hermetically sealed container for 20 days at atmospheric pressure at a temperature of 20-30° /26 and a relative humidity of 27-73%. The caloric content of the food was 2,500 kcal. During the entire study, water was consumed by the subjects on an ad libitum basis. Data on water consumption under these conditions are presented in Table 2.

TABLE 2.* DAILY CONSUMPTION AND EXCRETION OF WATER (IN LITERS) BY AN INDIVIDUAL IN A HERMETICALLY SEALED CABIN (DATA FROM 4 EXPERIMENTS) (After Morgan, 1962)

| Consumption | | | | Excretion | | | | Degree of imbalance |
|---|---|---|---|---|---|---|---|---|
| Drinking water | With the food | Metabolic water | Total amount | With the urine | Condensate | With the feces | Total amount | |
| 1,480 | 0,272 | 0,270 | 2,026 | 0,703 | 1,353 | 0,073 | 2,129 | —0,105 |
| 1,280 | 0,308 | 0,271 | 1,859 | 0,806 | 1,092 | 0,948 | 1,946 | +0,082 |
| 1,456 | 0,279 | 0,270 | 2,005 | 0,805 | 1,203 | 0,046 | 2,099 | —0,094 |
| 1,780 | 0,236 | 0,233 | 2,249 | 1,050 | 1,271 | 0,008 | 2,329 | —0,08 |

*Note: Commas indicate decimal points.

It follows from Table 2 that the total amount of fluid that enters the organism, including metabolic water, amounts to an average of 2,200 ml. It should be mentioned that under conditions of a longer stay by an individual in a hermetically sealed chamber, water consumption may differ markedly from the amount used by an individual kept in isolation for a brief period of time. For this purpose, water balance was studied in three subjects who were kept for one year in a hermetically sealed chamber.

The food ration saw extensive use of dehydrated food products with a total caloric content of 3,000 kcal/day; the air pressure was 1 atm, the partial oxygen content was 20.2%, the temperature of the environment was 20°, the relative humidity was 70%. The water supply system in the one-year experiment was based totally on the regeneration principle. During the tests, a strict record was dept of the amount of fluid in the intake and outlet of the regeneration system as well as the levels of water consumption and diuresis of the subjects. The amount of water removed for analysis was also taken into account. This made it possible to study water balance in man in a closed volume over a long period of time. Data on water consumption and diuresis are shown in Table 3. It follows from this table that the amount of water used by the subjects daily in the course of a year varied from 3,030 to 1,932 ml. An interesting feature is the fact that there was a tendency toward a decrease in the amount of water used by the subjects, with a slight rise in diuresis.

TABLE 3. DAILY WATER CONSUMPTION AND DIURESIS IN SUBJECTS DURING A ONE-YEAR EXPERIMENT

| Subjects | Nov. | Dec. | Jan. | Feb. | Mar. | Apr. | May | Jun. | Jul. | Aug. | Sep. | Oct. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Consumption, ml | | | | | | | | | | | |
| U | 2330 | 2326 | 2337 | 2207 | 2102 | 1950 | 1932 | 1934 | 2012 | 1986 | 2062 | 2040 |
| M | 2600 | 2406 | 2360 | 2090 | 2038 | 1951 | 1969 | 1995 | 1935 | 1992 | 2102 | 2000 |
| B | 3030 | 2703 | 2758 | 2502 | 2499 | 2475 | 2264 | 2242 | 2074 | 2142 | 2327 | 2222 |
| Average | 2653 | 2480 | 2485 | 2266 | 2211 | 2125 | 2055 | 2057 | 2006 | 2040 | 2163 | 2087 |
| | Diuresis, ml. | | | | | | | | | | | |
| U | 1320 | 1220 | 1170 | 1380 | 1450 | 1520 | 1580 | 1650 | 1600 | 1700 | 1870 | 1860 |
| M | 1250 | 1400 | 1477 | 1620 | 1540 | 1590 | 1610 | 1688 | 1610 | 1656 | 1521 | 1570 |
| B | 1425 | 1510 | 1430 | 1750 | 1700 | 1870 | 1570 | 1723 | 1920 | 2000 | 1746 | 1608 |
| Average | 1335 | 1380 | 1400 | 1580 | 1560 | 1588 | 1651 | 1687 | 1710 | 1785 | 1712 | 1680 |

The results of the spaceflights of the "Vostok", "Voskhod" and "Soyuz" spacecraft, as well as the experience in conducting brief and long experiments, has shown that the standard amount of water (2.2 liters) allows optimum working capacity and a high degree of psychological and physiological stability of the cosmonauts. However, if we take into account the individual characteristics of /27
the cosmonauts' organisms, the possibility of an increase in their emotional and physical stress, as well as the emergency situations, the calculated and optimal standards for water consumption per individual during a flight work out to 2.5 liters a day (Yezdovskiy, 1966; Biryukov, 1967; Grigor'yev, 1970; Kozyrevskaya, 1970, and others).

## Storage of Drinking Water

The problem of storing supplies of drinking water without its properties changing has faced scientists repeatedly in connection with supplying human beings with water under a number of specific conditions involving activity on Earth. The necessity of providing water supplies aboard ship and particularly during prolonged, isolated existence of submarine crews has caused researchers to be faced with the problem of finding new, reliable means of water storage.

In supplying water to expeditions, geological parties and sometimes larger groups of people, working in the desert or in other arid regions, it was necessary to devise a number of methods that would provide for storage of drinking water. The carrying out of these measures had to ensure that the chemical composition of drinking water would remain constant even under unfavorable climatic conditions.

Of course, similar requirements are imposed on water supply systems for spacecraft and stations, where drinking water, stored in hermetically sealed containers, must not change its chemical composition under the influence of a number of spaceflight factors. Naturally, preparations that are widely used for decontamination of water, such as chlorine, sulfur, etc., were the first to be tested for preservation purposes. /28

Tests that were performed involving the preservation of water by using high concentrations of chlorine (20-50 mg/liter) showed that residual chlorine remained in the water for 38 days and ensured total bacteriological safety for this period of time.

The shortcomings of this method of preservation include a marked change in the organoleptic properties of the water, noticed during the first 16 days (the odor and taste reached levels of 4-5 points) (Sologub, 1963). We know that the threshold for detection of free chlorine by taste is 0.5-0.75 mg/liter, while it can be smelled at 0.3-0.5 mg/liter (Cherkinskiy, 1962).

The study of the possibility of the penetration of active chlorine into water from porous vessels (Chamberlain candles, filters made of porous ceramics) have shown that this method is not very suitable. Adding chlorine to Zdravkov vessels made it possible to prolong the water storage period up to four months.

The purpose of all of these experiments was to ensure uniform addition to the water within the entire period of storage and to eliminate the possibility of high concentrations during the first few days. However, in conjunction with the decrease in the volume of water, an increase in odor and taste was observed in this instance from 2-4 points in three months.

L. Voytkevich, Ye. Mishustin and Ye. Runov (1926), in studying chlorinated water that had been stored for a long period of time and had a residual chlorine content of 0.1-0.5 mg/liter, established that when microflora entered this water for the second time there was a more rapid multiplication of microorganisms than was in the case with unchlorinated water.

K. K. Boglyubov (1943) felt that even superchlorination in doses up to 150 mg/liter is unsuitable for prolonged storage of water, since protection is not guaranteed against secondary contamination and development of microorganisms is sometimes enhanced under these conditions. The authors feel that the rapid development of microorganisms in chlorinated water may be explained either by the stimulating effect of small amounts of chlorine or by the absence of microbial antagonists. Taking all of these facts into account, S. I. Slonevskiy (1943) proposed that chlorine for the preservation of water be added at the rate of 0.5-1.0 mg/liter of active chlorine once every five days at temperatures of +18-25° and once every seven days at lower temperatures.

D. I. Kuz'min (1956) stored water in a container made of rubberized cloth under the conditions of water supplies in the field. As a preservative, he

used chloride of lime and ammonia. The chlorine dose was 20, 25 and 50 mg/ /liter, with various weight mixtures with ammonia. The use of rather high doses of chlorine was due to the high chemosorptive properties of the rubberized cloth and the storage periods (10-15 days). Tests showed that when water is stored for this period of time the necessary doses of chlorine are at least /29
20 mg/liter with 20 mg/liter of ammonia, i.e., in a ratio of 1:1. It must be pointed out that when storing water either with a preservative or without it in a bag made of rubberized cloth, there is a deterioration of the physical characteristics and chemical properties. However, in tests without the preservative, the changes occurred earlier and were more pronounced. The author suggests the possibility of using chloride of lime together with ammonia for preserving water in rubberized cloth as the simplest, easiest and most effective means for brief storage under sealed conditions.

Nevertheless, chlorine preparations have not seen extensive use for preserving water. The main reason is that it is necessary to use high doses of chlorine which considerably modify the organoleptic properties of the water, and in the second place there is the possibility of a development of strains of microorganisms that are resistant to chlorine which can grow while the water is stored.

Decontamination of Drinking Water by Silver Ions

Among the reagent methods that have been proposed for decontamination of water, one of the most important involves various silver preparations. Silver solutions were used for decontamination in ancient times. The bactericidal properties of silver, like certain other metals (copper, mercury), with respect to water plants were first observed by Nagely (1893) during the 1890's. He introduced the idea of "oligodynamia". This term means the action of metals and their salts in such dilutions that investigators were unable to detect the presence of the metals themselves by chemical methods. Even the works of the very first researchers who examined the oligodynamics of silver recorded very important facts: in the first place, the oligodynamic effect could be transferred to water, and secondly, according to the original findings of Nagely, water that had been subjected to the oligodynamic effect could be found to contain traces of metal, and in the third place, the existence in the water of substances that were capable of absorbing metals on their surfaces, led to the weakening or disappearance of the oligodynamic effects. These same works established, however, that the actual cause of oligodynamia is the metallic silver ion. P. Ye. Yermolayev (1935-1936), I. F. Aleksandrov (1935), Ye. A. Plevako (1936) and others showed that the action of destroying bacteria with silver is caused by the transition to the ionic state of dissolved compounds of the metal that form on its surface in the course of processing and manufacturing the metal, as a result of exposure to air, or due to the effect of certain oxidizers. To prove this, the researcher placed a sheet of metallic silver in a Petri dish containing agar, which had previously been inoculated with Escherichia coli. In the event that the dish had not been washed out /30
beforehand to get rid of an oxide film and silver salts, growth of microorganisms was not observed around the sheet for 48 hours. The experiments of S. V. Moiseyev (1932) also confirm this finding.

The study of the properties of the various compounds that are formed on the surface of metallic silver ($Ag_2O$, AgCl, AgBr, $Ag_2S$) has shown that only the sulfide film which very frequently forms in the course of the interaction of silver with air containing hydrogen sulfide has no bactericidal effect. In addition, the oligodynamic effect of silver may depend on the physical state and the chemical properties of the metal itself. Thus, plastic deformation slightly increases the chemical activity of the metal (Klochkov, Kunina, 1960).

A number of authors (Yermolayev, 1935; Plevako, 1936; Lazarev, 1936) have suggested that the bactericidal properties are not inherent in the contact metal silver, but in its compounds which are soluble in ammonia. They have suggested that under the conditions that exist in a living organism, ammonia is the only solvent of silver compounds. Wherever living organisms are found, ammonia will be found as well. The ammonia solutions of silver compounds which are formed are capable of penetrating the bacterial cell, causing its death. To support their theory, they present the following experimental data. If silver nitrate, which is soluble in water, has a bactericidal effect at a dilution of $1:10^{-9}$, $AgNO_3$ + 5 $NH_3$ will have the same effect at a dilution of $1:10^{-17}$, and $AgNO_3$ + 10 $NH_3$ will show this effect at a dilution of $1:10^{-90}$. The numerous papers of Slavin (1935, 1937), Aleksandrov (1935), Los' (1936), Stolmakova (1939), Moiseyev (1932) and Dmitriyev (1933) have shown, however, that ammonia which is not taken in a bactericidal dose will not improve the bactericidal properties of silver and even has a tendency to reduce them. This is due to the fact that most of the silver which is dissolved in the organic medium is in the form of complex compounds and only an insignificant part occurs in the form of free ions. Ammonia produces a complex ion with silver and therefore is completely incapable of keeping silver in the ionic state. In order to compensate for the reduced concentration of free ions in these compounds, it is necessary to increase the total dose of complex silver by hundreds of thousands of times.

It may be assumed that other disinfectants were active in the experiments of Yermolyayev and Lazarev. Thus, the content of active chlorine in some of Yermolayev's experiments was 0.2-0.3 mg/liter (Slavin, 1937).

The studies of Kul'skiy (1962, 1963) and a number of other papers state that it is the ions of the metals which cause the death of the microorganisms. The mechanism of the action of silver on microorganisms was viewed by Slavin (1937) and Moiseyev (1932) as a process that takes place in two stages: an initial one (reversible) which consists of the absorption of silver by the surface of the bacterial cell, and a second (irreversible) which involves the combination of the protein in the bacteria with the silver ions. As far as the influence of ionic silver on the bacteria directly is concerned, there is /31
no unanimity of opinion on this point at the present time.

The theory of Vorats and Torfen (1957) is the most interesting and widely accepted one. According to this theory, silver ions block active groups of bacterial enzymes (for example, sulfhydryls) and inactivate them (Braune, 1957). This causes breakdown of metabolism and death of the microorganisms.

As to the amount of dissolved metal required to produce the bactericidal effect is concerned, the researchers have not always come to the same conclusions. The degree of activity of silver increases with the concentration of its ions in the solution. At the same time, however, it depends on a large extent on the physical and chemical properties of the water.

The work of Kul'skiy (1962, 1963, 1968), has demonstrated the distinct dependence of the bactericidal effects of silver on the concentration of its ions. Thus, a silver dose of 0.05 mg/liter made water contaminated with 50,000 microbial bodies of E. coli per liter decontaminated the water in 1-2 hours and 0.5 mg/liter decontaminated it in 30-60 minutes. Increasing the temperature and raising the alkalinity of the water promoted the bactericidal effect. According to the data of Kul'skiy and his associates, heating the water from 0 to +10° increased the bactericidal action of silver four times at an exposure time of 30 minutes, and 200 times with an exposure of 90 minutes.

Wuhrmann (1958) also points out that increasing the temperature by 10° speeds up the death of the bacteria by 1.6 times. The salt composition of the water in turn has a significant influence on the decontamination process, particularly when ions are present which convert the silver to slightly soluble compounds. These include in particular the chlorides and sulfates which occur widely in natural waters. Since the amount of free silver ions in this case is decreased considerably, there is a decrease in the rate of decontamination as well. However, when there is an excess of silver chloride, this decrease is not proportional to the decrease in the silver ion concentration, since silver chloride slightly increases the disinfectant action. An increased content of Cations in water is accompanied by a slight rise in the threshold of the bactericidal effect and a reduction in the time required for the bacteria to die off. The effect of other impurities contained in drinking water, such as $NH_4^+$ and $SO_4^{-2}$ on the bactericidal effect of silver is low (Kul'skiy, 1968; Konrich, 1929; Olszewskiw, 1935).

A considerable influence on the effectiveness of water decontamination by silver is exerted by the number of microorganisms contained in the water. We know now that silver has a significant bactericidal effect which makes it (in the opinion of several authors) a stronger disinfectant than carbolic acid and bichloride of mercury (Yershova, 1938; Kul'skiy, 1963). As far as the effectiveness of the action of water containing silver on bacteria is concerned, the latter may be ranked as follows: E. coli, Bact. dysenterie, Flexner, Bact. typhi abdominals, Streptococcus, Staphylococcus. It should be pointed out /32 that pathogenic organisms are generally more sensitive to the effect of silver than the saprophytic bacteria are.

The sensitivity of individual species of microorganisms to silver ions is so different that attempts have been made to use this property to distinguish between similar species (Dmitriyev, 1939). Escherichia coli is most sensitive to water containing silver; for this reason, it was used as the indicator in most studies.

Plevako (1936) showed in his work that a silver dose of 0.04 mg/liter causes decontamination of water containing E. coli in an amount of 10 microbial bodies per ml.

The work of O. S. Savluk (1969) and others has shown that silver has a significant influence on various viruses, including the $A_1$, $A_2$ and $A_{265}$ flu viruses. Solugub (1963), Fyrshirotu, Koniver and Vorovik (1960) studied the effects of silver on 11 species of microorganisms. However, the silver concentration which they employed (250 mg/liter) was ten times greater than the dose which would ensure a bactericidal effect in the works of other authors and for this reason is incomparable with other works in this area. Kul'skiy (1968) and his associates studied the oligodynamic effect of silver on 17 species of organisms, including various representatives of the intestinal microflora, both pathogenic ones (S. paratyfi A-209, S. dysentriae Flexner), air microflora (strains of staphylocci, resistant to the effects of antibiotics). The non-sporogenic gram-positive and gram-negative bacteria were found to be the most sensitive to silver. A silver dose of 0.2 mg/liter was found to be sufficient to decontaminate water containing $10^2$ microbial bodies per ml. It is precisely because the bactericidal effect of silver is a function of the physical and chemical properties of the medium and the degree of bacterial contamination, that various authors have proposed using various doses to decontaminate water.

In the experiments of Dmitriyev (1933) involving decontamination of river water, in order to achieve the necessary bactericidal effect it was necessary to use about 75 micrograms of silver per liter (0.075 mg/liter) with an exposure time of 2 to 24 hours. However, Los' (1936) and Aleksandrov (1935) consider that the active doses needed for decontamination of river water amount to 1 mg/liter or more. On the basis of these studies, they propose that concentrations of 0.5, 1.0 and 2.0 mg/liter be used for treating water supplies in the field. In many experiments, doses of 0.1-1.0 mg/liter turned out to be bactericidal at practically acceptable times (Garbarenko, 1938). The studies of a number of authors have shown that extremely low silver doses, on the other hand, stimulate the growth of bacteria (Bashtan, Slavin, 1935).

Several methods of enriching water with silver ions have been developed as of the present time.

Method of Contact With Silvered Surfaces /33

In 1928, Georg Krauze proposed that metallic silver, finely dispersed or precipitated on an object with a large surface, be used for the decontamination of water. Uglov (1933) recommended that silvered glass dishes be used for this purpose. The experimental data which he presented showed that when a culture of E. coli was placed in tap water (1 bacteriological loop per liter) and stored in a silvered flask, this water became sterile in 4 hours. Repeated studies of the decontaminated water for 7 days showed a complete absence of microbial contamination.

Korotchenok and Krepkogorskaya (1934) also studied the possibility of decontaminating water in silvered dishes. For this purpose, a culture calculated to contain 100,000 microbial bodies per ml was placed in a vessel with a capacity of 15 liters. A decontaminating effect was observed in one hour, while using vessels with a volume of 5 liters allowed the water to be

decontaminated in 3 hours. It may be assumed that the increase in decontamination time in small vessels is due to the lower concentration of dissolved ions. In order to ensure a more rapid transfer of silver ions to the solution, it has been suggested that the metal be applied to larger surfaces (necklaces, Rasching flasks, powdered carbon, etc.). In the Soviet Union, Uglov (1933), has suggested silvered sand for sterilization of drinking water. Sand which has been silvered with a 2% solution of silver nitrate was used for filtration of contaminated water at the rate of 120 cc/minute; it caused the death of E. coli in 3 hours and killed the agents of typhus abdominalis and dysentery in 2 hours. At the same time, the controls were found to contain viable microorganisms. Unfortunately, the initial concentrations of microorganisms in the solutions were not mentioned in these papers, so that it is difficult to evaluate the degree of the bactericidal action.

V. A. Uglov developed so-called "black" silvered sand by converting metallic silver to the oxide for the purpose of increasing its bactericidal properties. S. V. Moiseyev (1932) made and tested 145 samples of silvered sand. Some of the samples of silvered sand yielded practical results in terms of decontamination that were many times greater than those achieved with chlorination.

A comparative study of "black" sand and No. 56 sand in terms of its effect on a suspension of E. coli in tap water showed that the black sand was better; it produced total sterilization immediately after filtration, while the effect of decontamination following passage through No. 56 sand took place much later. I. F. Aleksandrov (1935) obtained similar results but he also noticed some negative aspects of the black sand.

Pure tap water became cloudy, took on a pink color and acquired an unpleasant taste 15-20 minutes after filtration. The study of the bactericidal /34
activity of black sand under dynamic conditions revealed that it underwent a gradual weakening as the water samples being investigated were being filtered. Thus, while the percentage of organisms killed in the first five liters was 99.7, it was 99.93 in the second five liters and so on, so that after 50 liters had passed through, it had decreased to 65%. Hence, filtration of large volumes of polluted water revealed a weakening of the bactericidal action which necessitated constant bacteriological monitoring.

In decontamination of water contaminated with cultures of E. coli, using filtration through metallized carbon at the rate of 60 cc/minute, immediately after filtration the number of bacteria fell by 77-80% and was down 95-98% after an hour (Los', 1936). The author noted that the bactericidal properties of silvered carbon changed as a function of the type of water and always decreased following filtration of large volumes of water.

Regardless of the unanimous confirmation of the high bactericidal action of various silvered filtration preparations by researchers, this method has not come into wide use. The reasons for this consist mainly of the following: the impossibility of accurate silver dosage and consequently the danger of high doses, the need to maintain a contact time with the silvered surface in

each concrete case as a function of the physical and chemical composition of the water and the degree of microbial contamination.

Method of Decontamination Using Silver Salt Solution

This method has been discussed rather fully in the literature. Silver nitrate, ammonia solutions of silver, ammargene, oligodine and other preparations have been used for decontaminating water.

S. A. Dmitriyev performed an experiment involving the decontamination of river water in 1933 (the Don, Kamenka and Psekups rivers) using a 0.1% solution of silver nitrate; he observed a pronounced bactericidal effect. However, a comparative study of the bactericidal action of silver salts and other decontaminating agents, particularly chlorine, has led several investigators to conclude that silver is weaker in its action than chlorine. Thus, V. D. Slavin (1937) feels that chlorine has an advantage over silver in the decontamination of distilled water. In his experiments, a concentration of 1 mg/liter of silver nitrate killed Escherichia coli (100,000 microbial bodies/ml) in 30 minutes; a concentration of 0.1 mg/liter killed them in 2 hours, while 0.05 mg/liter had no effect even after 24 hours. Chlorine on the other hand, given at a dose of 0.1 mg/liter, achieved a sterilizing effect in 10 minutes and a dose of 0.05 mg/liter achieved the same thing in 1 hour.

No impertinent difference in bactericidal action between various silver salts has been found (Los', 1937). The method of water decontamination using silver salts has not been recommended for extensive usage because of its cost /35
and insufficiently high bactericidal action. However, in the course of working with these preparations, it has been found that silver may have considerable advantages over other disinfectants in cases when prolonged storage of decontaminated water is required, since silver has the ability to retain its bactericidal properties for a long period of time when added to water. Thus, Polak (1959) points out that silver nitrate used in doses of 0.05-0.1 mg/liter retains its bactericidal effect for 25-30 days. In this connection, silver salts at doses of 0.5, 1.0 and 2.0 mg/liter have been recommended for storage of water under field conditions (Dmitriyev, 1963).

Gabovich (1939) recommended that silver nitrate be used at the rate of 0.5 mg/liter for conservation of water for 5-10 days, while a dose of 1.5 mg/liter will preserve it up to a month. The duration of the bactericidal effect is a function of the original condition of the water. Silver nitrate at a dose of 0.5-1.5 mg/liter will reliably preserve clear pure water with a negligible content of organic matter (permanganate oxidability of 1-2 mg $O_2$/liter) and a chloride content of no more than 50-70 mg/liter. Water with a high organic matter content is preserved poorly by silver salts, even at concentrations up to 2 mg/liter (Aleksandrov, 1935; Los', 1936).

In addition to silver nitrate, a number of other preparations have been suggested for the decontamination and preservation of water. Thus, a preparation called oligodine was manufactured in Germany for preserving water in water bottles (Krotkov, 1942).

In recent years, the firm of Angelmi Werken has proposed that a preparation called kumazin be used for decontamination and preservation of water aboard ship. Recommended doses for decontamination and preservation were 50-100 mg/liter, with a silver content being 0.01 to 0.04 mg/liter, respectively (Borgolte, 1943).

Experiments performed by Uhleman (1958) have shown that 6 hours after the preparation was added to tanks containing drinking water the coli titer was more than 100.

In experimental studies performed by N. A. Rakhmanina and V. A. Druzhinina (1962) it was found that the coli titer rose from 0.0004 to 111 in one hour with kumazin concentrations of 50 and 100 mg/liter. The total amount of bacterial metatrophs fell from 250-300 to 50-90. In 24 hours the coli titer of the decontaminated water was 333, while the total amount of bacteria was no more than 2-14. The preserved water retained its high bactericidal effect for all 30 days of the test. An adequate with a kumazin concentration of 25 mg/liter was obtained only for the 6 days of contacts. While in the studies of Rakhmanina and Druzhinina the effectiveness of preservation using kumazin was studied at temperatures of +18-20° in a glass container, P. M. Litvinenko and B. U. Alamyarov (1966) observed this process under conditions of a hot climate while storing water in rubberized, glass and metal containers.

The sanitary-hygienic evaluation of the preserved water required 30 days. /36
One hour after addition of kumazin to the water the coli titer rose from 0.04 to 100-200, reaching 333 in 24 hours. In the course of 30 days, water in glass and metal containers retained good organoleptic and physical-chemical properties. However, the authors do not present complete physical and chemical analytical data on the preserved water. Deterioration of the organoleptic and bacteriological parameters of the preserved water were observed only in the case of the rubberized cloth.

On the basis of their experiments the authors recommend using kumazin for the preservation of drinking water for periods from 30 days at doses of 25 and 50 mg/liter, i.e., smaller doses than those recommended by Rakhmanina and Druzhinina. It may be assumed that this has to do with the fact that the bactericidal action of silver increases as the temperature rises.

Hence, it follows from the above that various silver salts have been used successfully for the preservation of drinking water for periods up to 30 days. However, this method does have shortcomings which include particularly the addition to the water of undesirable impurities along with the silver ions: nitrates, ammonia and so forth. This has forced the investigators to direct their attention to the possibility of adding silver ions to water by means of electrolytic decomposition of silver electrodes.

Electrolytic Method

The first experiments aimed at obtaining silver solutions by the electrolytic method were performed by L. A. Kul'skiy in 1930, and in 1932 a paper by R. Krauze was published containing similar data. Kul'skiy found that when

D.C. was passed through a pair of silver electrodes submerged in water, silver ions from the anode were transferred to the solution. He determined the most efficient conditions for obtaining ionic silver solutions: the distances between the electrodes should be 5-12 mm, the current density should be 0.5-5.0 mA/cm$^2$ and the applied voltages 3-12 V. In 1935-1948, working in the Laboratory of Water Purification Technology of the Academy of Sciences of the Ukrainian SSR, L. A. Kul'skiy, A. M. Koganovskiy, O. K. Lebedintseva and others showed that the nature of the process is a function of both the salt composition of the water and the electrolysis conditions. When there is a large quantity of chlorides in the water a film of silver chloride forms on the anode, and disturbs the passage of ions into the solution. Carbonates, sulfides and phosphates have effects similar to those of chlorides. When there are large quantities of sulfates in the water, the input of ionic silver is reduced due to the liberation of oxygen at the anode. The distance between the electrodes, the concentration of the current and the temperature of the solution all affect the silver yield.

In 1953 workers at the Ukrainian Institute of Communal Hygiene tested the bactericidal effects of electrolytic solutions of silver. The experiments /37
were performed with water from the Dnepr River (total number of bacteria per ml was 936 with a coli titer of 0.1); this water had come through the water supply system, been sterilized and then contaminated with intestinal bacilli (coli titer 25.0 and coli titer 0.01). Ionic silver was added to the water being studied at the rate of 0.2 and 0.06 mg/liter. At a 0.2 mg/liter dose of ionic silver the coli titer was more than 211 in all of the samples after 30 minutes and the total microbial count was 0. A dose of silver of 0.06 mg/liter ensured similar results with a contact time of 120 minutes. The authors drew a general conclusion that the method was highly effective for the decontamination of water. An evaluation of the bactericidal properties of water containing silver ions at a concentration of 11.6 mg/liter, performed in pure cultures of microorganisms, intestinal and pharyngeal microflora and 12 strains of Proteus pyogenicus, showed that water containing silver had a bactericidal effect on pure cultures of gram-positive bacteria in 30 minutes at a concentration of 100 million microbial bodies per ml and in 24 hours with one billion microbial bodies per ml (Brezgunov, Lipin et al., 1964). The authors found that water containing silver has bactericidal effects on microflora from the intestines of children, containing enteropathogenic intestinal bacilli and other gram-negative microorganisms, in 30 minutes with a content of one billion microbial bodies per ml. The bactericidal action on a culture of B. proteus vulgaris at a concentration of 10 million bodies per ml using water containing silver was evident in 60 minutes.

A. I. Stolmakova and E. S. Turetska (1949) conducted tests involving the study of the bactericidal action of water containing silver with concentrations in the range from 0.01 to 10 mg/liter. The test microbe was a culture of E. coli at a concentration of 100,000 microbial bodies per ml. In distilled water, containing 0.1 mg/liter of silver, a pure culture of intestinal bacilli was killed in 15 minutes, while at 0.1 mg/liter, after 15 minutes of contact, individual colonies were still growing. However, the control showed tens of thousands of microorganisms. In the case of decontamination of water from the

Poltva River using doses of 1 and 2 mg/liter, no visible effect was seen after 30 minutes. This is explained by the fact that the river water contains a large amount of organic substances in whose presence the bactericidal effect was reduced. Water from this same river has a chromaticity of 60°, a transparency of less than 2 cm, and ammonia content of 3.5 mg/liter, nitrite content of 0.2 mg/liter and 65 mg/liter of chlorides. The permanganate oxidability varied from 35.8 to 352 mg $O_2$/liter.

S. S. Dyachenko, V. Ya. Pochinok and Ye. P. Podrushnyak (1963), studying the antibacterial properties of water containing silver, concluded that silver had a mild bactericidal effect at doses of 10.5 and 2.5 mg/liter. Artificial contamination was performed using various cultures of microorganisms at the rate of 50 million microbial bodies per ml of water. The effect was evaluated after 30 minutes and after 24 hours following the start of this contact. The authors feel that ionic silver at a concentration of 5 mg/liter has an antibacterial action with respect to E. coli, the agents of dysentery and typhoid fever, as well as staphylococci; however, this effect is seen only after 24 hours. After 30 minutes the bactericidal action of silver could not be seen even at a dose of 10 mg/liter. Checking these data, L. B. Dolivo-Dobrovol'skiy (1958) showed methodological errors in the performance of the experiments. First of all, the dose of microorganisms used for contamination was too great and the microbes themselves were not in water but in a 1% solution of glucose. The presence of organic substances in the bouillon sharply reduced the bactericidal effects of the silver. Cultures of microorganisms were grown for only 30 minutes and 24 hours, so that there was no possibility of establishing the required time of contact to achieve bactericidal effects in this case. Only complete death of all the existing microflora was accepted as a positive effect. On the whole, however, the data from Soviet and foreign authors that have been presented in recent years confirm the high bactericidal properties of electrolytic solutions of silver (Kul'skiy, 1968). This is due to the fact that ionic silver is being used to an increasing degree for the decontamination of water. Many European companies (Angelmi Werken, Comega and others) are producing "ionators" with various degrees of efficiency, recommending them for the decontamination of water in small water supplies, at sanitoria, hospitals and in those places where the use of chlorine is undesirable or requires prolonged storage of water (Stuchlek, 1960; Polak, 1959; Ohone, 1959; Walter, 1962; Yoetz, 1943; Brunner, 1950; Obrezill, 1957). Recently the method of decontaminating drinking water by using silver has been employed in a number of city water supplies in Iran and West Germany (Braune, 1957) and also for treating water in swimming pools in Czechoslovakia and the Soviet Union (Kozirowski, B., 1961; Kharshat, 1962).

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It is quite natural that considerable interest has arisen among investigators concerning ionic silver as a preparation with a prolonged effect that would allow the possibility of prolonged storage of drinking water. The experiments of Kul'skiy et al, (1962) involving storage of drinking water treated with electrolytic solutions of silver (0.2-0.4 mg/liter) established that water remains potable for 5-6 months without deterioration of its properties. At the end of the storage period the silver concentration was found to have fallen to 0.05-0.1 mg/liter. Treating water with silver for prolonged storage aboard ship was recommended by Wooldward (1963) and Walter (1962).

Successful experiments aimed at the decontamination and preservation of drinking water by using silver ions have been a prerequisite for the performance of investigations involving the study of the possibility of sterilization of beverages by this method. V. D. Slavin (1937) feels that "oligodynamia" is not suited for purposes of sterilization of beverages. Since the active element is the free ion of the metal, in a medium which is rich in protein substances the production of compounds that are weak as far as dissociation is concerned (complex ions) sharply deteriorates the bactericidal effect. To compensate for the reduced concentration of free ions in complex compounds it is necessary to increase the total dose hundreds and thousands of times. Thus, for the sterilization of milk this same author suggests a dose of at least 100 mg/liter for a contact time of 3 hours. /39

The works of Stolmakova and Turatska (1949) have shown that the concentrations of 2.0, 4.0 and 6.0 mg/liter cannot be used for preservation due to the change in the organoleptic properties of the milk. Doses of 1.0 and 2.0 mg/liter failed to achieve sterilization even after 4 hours.

Experiments involving the preservation of tomato juice also yielded negative results. The preservative effect in this case was provided by a dose of only 6 mg/liter, but it sharply modified the taste. The study performed by P. S. Klasel'man (1947) of the preservative properties of electrolytic solutions of ionic silver as they apply to milk, butter and powdered eggs demonstrated the possibility of stabilization of milk in winter for up to 4-5 days by 6-8 mg/liter of ionic silver. To stabilize butter, concentrations of at least 2.2-3.75 mg/liter are recommended. Most authors, however, conclude that it is impossible and inadvisable to use water containing silver for preserving food products or for disinfecting only slightly decontaminated water.

Hence, on the basis of an analysis of the data in the literature and certain preliminary conclusions drawn in articles on this subject, methods of preservation of water were worked out for water supply systems designed on the basis of water reserves for the entire duration of the flight.

However, the problem of developing methods of water preservation arises in conjunction with water supply regeneration systems. This problem becomes more pressing since the designs of the proposed water supply systems involve increased usage of new polymers, coatings, plastics and other materials. It is necessary to take into account the wider temperature range in which these proposed systems of water supply can be used.

In view of the fact that the functioning of the regeneration systems for water supplies in a closed space creates highly favorable conditions for the growth and development of new species of bacteria, which are capable for example of intensifying the process of hydrolysis of urea, special attention should also be paid to the development of methods of preservation and decontamination that work on the flow of fluid.

The problems involved in working out methods of preservation of water must be closely linked to problems of decontamination. It has been found that

during prolonged storage or extensive usage of water supply systems there is an intensive development of flora on the internal surfaces and in the technological elements of the system.

Hence, in proceeding further with the solution to the problem of water preservation, the principal task will be the study and choice of such preservatives as will ensure high physical-chemical and bacteriological characteristics of water without toxic properties during prolonged storage of water under appropriate conditions. /40

The preservative action of silver preparations have been studied in connection with the storage of water in glass vessels and in vessels made of polymer materials on the basis of generally accepted methods of sanitary hygienic evaluation of water. In various stages of storage we studied the bactericidal properties of the preserved water by means of artificial contamination of the water samples with a culture of E. coli at doses of 1,000 and 10,000 microbial bodies per ml. The preservative effect of kumazin was studied at doses of 0.05-0.1 g/liter; silver nitrate at 1.5 and 2.0 mg/liter and ionic silver at 0.1, 0.2 and 0.5 mg/liter. The duration of storage of drinking water in a glass container was 18 months while in a container made of polymer materials it was a year.

The studies that were performed showed that in the case of prolonged storage of drinking water in a glass container there was a difference in the physical-chemical properties of the water as a function of the type of preservative. Thus, when kumazin was used the preserved water was found to have an accumulation of nitrites whose amount was about 40 times greater than the original value after a year of storage, and a direct relationship between the increase in the nitrites and the dose of the preservative was found. In addition, water that had been preserved with kumazin showed an increase in chlorides and a rise in oxidability which may be explained by the presence of organic substances containing chlorine in the preparation.

The physical-chemical parameters of drinking water preserved by silver nitrate and ionic silver did not undergo any noticeable changes during storage. There was only a slight increase in nitrogen from nitrates in the water preserved with silver nitrate, associated with its inclusion in the preservative. However, the quantity of nitrates did not exceed the requirements of the All-Union State Standard. These preparations, when used for storage of water in a glass container, ensured total retention of the original organoleptic properties of the water. In the course of bacteriological investigations of water samples that were stored for a long period of time and had been preserved with kumazin or silver nitrate, no viable microorganisms could be found.

The studies we carried out involving storage of water in a polyethylene container after adding kumazin showed that the organoleptic properties of the latter underwent considerable changes. The odor and taste at the end of the first year were rated at 3 points, while in the case of storage in a glass container these parameters did not change. At the same time, there was an increase in oxidability, amount of ammonia and nitrogen from nitrites. However, in the case of 6 months' storage these parameters did not exceed the

limits of the sanitary-hygienic standards for drinking water, but after a year of storage the nitrogen content from nitrates (0.28 mg/liter) was considerably in excess of the requirements of the All-Union State Standard. The increase in oxidability was seen also in the case of storage of water preserved with ionic silver in a container made of polyethylene; we used different brands ("Alkatene," "saran," high-pressure polyethylene). Increasing the dose of the preservative led to a more pronounced increase in oxidability which was the consequence of destructive changes in the film. The latter caused a penetration of organic acids of the paraffin series into the water, which was established by studying the precipitate by means of spectral analysis. In addition to the increase in oxidability, there was a slight deterioration of the organoleptic parameters. However, in the course of 6 months of storage in a polyethylene vessel, with the water being preserved with 0.1 mg/liter of ionic silver, all of the changes of a physical-chemical nature fell within the limits allowed for drinking water (Sitnikova et al., 1972). /41

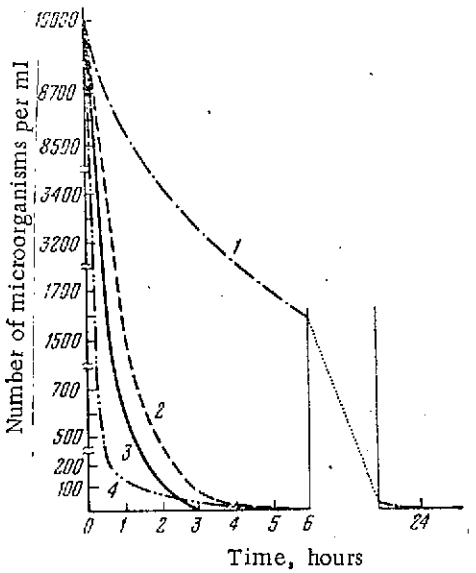


Figure 1. Dynamics of the Death of E. coli in Drinking Water Containing Various Concentrations (in mg/liter) of Silver.
1, 0.1; 2, 0.2; 3, 0.5; 4, 1.5.

Hence, our studies of the preservative properties of various silver preparations have shown that kumazin, silver nitrate and ionic silver make it possible to store water for 6 months in glass and polyethylene vessels. However, the best stabilization of the original characteristics of drinking water is provided by the use of ionic silver.

The study of the bactericidal effects of various preparations of silver reveals their high effectiveness. Even in the first hour following addition of a culture of E. coli to the water, death of 84-96% of the introduced microorganisms was observed. After 6 hours, in all investigated water samples, all existing microflora were found to have died (Figure 1).

Artificial contamination of water samples revealed a slight decrease in the bactericidal activity of the preserved water as the storage time increased. When E. coli was added there was a remarkable change in the dynamics of development of microorganisms (up to 24 hours) and the process of water sterilization was prolonged. Using the example of ionic silver it was apparent that this is due primarily to the small doses of preservative (0.1 mg/liter) and the very long periods of storage (up to 3.5 years). /42

It was found that by the end of this period of time the concentration of the ionic silver in the water samples had fallen 20 fold. This fact was evidently due to precipitation of silver on the inside of the vessel. Silver was absorbed more actively on the surfaces of polyethylene films, from which all of the soft containers of city water supply systems are made.

Despite the high bactericidal effect of all of these preparations of silver, we felt that we could recommend ionic silver as being preferred for purposes of preservation of drinking water aboard a spacecraft. This is due mainly to the fact that ionic silver, which has pronounced bactericidal effects, provides a long-term preservative effect and ensures stable physical-chemical and organoleptic properties of water when stored in glass and polyethylene containers.

The minimum effective dose of ionic silver is 0.1 mg/liter. Use of a smaller dose, 0.05 mg/liter for example, considerably reduces the bactericidal properties. On the other hand, during preflight preparation of the craft, lasting several days, the silver concentration in the drinking water may drop by an average of 20% due to sorption on the surface of the vessel.

Studies which we performed under conditions of autonomous and complex tests showed that the method of water preservation using ionic silver at a dose of 0.1 mg/liter ensures total preservation of sanitary-hygienic parameters of water within the limits of the time intervals provided for the flight program. The method was put into practice and used in supplying water to the crews of the "Vostok," "Soyuz" and "Salyut" spacecraft. The cosmonauts remarked on the good taste of the water. Sanitary-hygienic evaluation performed after the flights showed total stability of the original physical and chemical parameters.

Water Supply Systems for Crews Aboard the "Vostok" and "Voskhod" Spacecraft

In developing the water supply systems for the first spacecraft it was necessary to take into account that the system would have to have minimum weight, be hermetically sealed, withstand g-forces and vibration encountered during the active portion of the flight, and also be convenient for supplying water under weightless conditions. In addition, strict requirements were also imposed on the materials from which system elements in direct contact with the water would be made. These materials must not give off toxic compounds or substances that would change the chemical composition and organoleptic properties of the water. /43

In the water supply systems of the "Vostok" and "Voskhod" spacecraft the principle of using flexible containers was proposed; these containers would balance the pressure under weightless conditions, be made of polymer films or other elastic materials and would be housed in metal containers. The containers were made of several layers of polyethylene film, and contained in rubber and cloth bags for protection. All of the layers of the container were hermetically sealed to an internal branch of the nozzle which served as the base for fastening the system to the rigid container. The outside branch of

the nozzle was also hermetically fastened to a hose with a mouthpiece. The mouthpiece design incorporated a valve device which allowed water to be sucked out only when pressing a button on the device.

From the water supply system, the drinking water that had been preserved with a solution of ionic silver (concentration of 0.1 mg/liter) reached the cosmonaut by suction. To increase the reliability of the operation of the system in terms of decontamination and deodorizing of the water, a space in the mouthpiece was filled with activated charcoal impregnated with silver. The rarefaction produced in the oral cavity was completely adequate for the cosmonaut to be able to suck the water out of the polyethylene container (Sisakyan, Yazdovskiy, 1962).

One of the versions of the water supply system used for the "Vostok" and "Voskhod" spacecraft was a system incorporating a metal container with 2-layer polyethylene containers mounted inside it. The absence of a rubber container excluded the possibility of the characteristic taste of rubber entering the water.

The most important difference in this system was the provision of a device that would control consumption of water by the cosmonaut. The dispensing device, in the form of a special counter, made it possible to determine from its scale how much water had been drunk at the rate of 15-20 ml per portion.

## CHAPTER III: REGENERATION OF WATER

### Characteristics of the Construction of Systems for Water Regeneration Under Spaceflight Conditions

Several characteristics typify the construction of water supply systems based on regeneration processes under the conditions of actual spacecraft flights. A simple transfer of known methods for regeneration of substances, widely employed in the chemical industry or analytical practice, to specific spaceflight conditions will not provide a solution to the problem in question. Thus, methods such as extraction, rectification, flotation and a number of others which are employed in chemical technology cannot be used under weightless conditions. /44

On the other hand, effective methods can be used in space which have been rejected on Earth out of economic considerations, since it is possible to use costly materials in a limited application. In evaluating a particular method of water regeneration, one must take into account the strict requirements as to the energy consumption of the system.

The characteristics of the design of systems for recycling materials necessarily include the unusual difficulty of developing a single method of regeneration. For example, regeneration of water from fuel cells which give off moisture or reactors for decomposing hydrogen peroxide is practically unsuitable for use in a system for regenerating water from urine and other waste products. A method such as the radiation method, which uses little energy, is difficult to use on short flights due to the need for providing considerable protection against ionizing radiation. However, on long flights the radiation method would be one of the currently possible approaches. Methods of regenerating water that have been devised for conditions on the Moon are very difficult to use aboard spacecraft that are under weightless conditions.

In selecting a unit, catalyst, sorbent or other component for the regeneration system, it will be necessary to take into account the influence of the vibrational stresses that arise during the active stage of insertion of the craft into orbit or during its maneuvering. The development of a reliable means of regeneration that uses little energy and has been devised for terrestrial conditions still does not mean that it can be used in space. In some cases, its use may be limited by engineering and design solutions (for example, the difficulty of organizing a system for condensing water in a vacuum with a simultaneous output of the condensate under weightless conditions). Consequently, it is necessary to devise a broad range of methods from which we can select the most suitable ones for each specific goal. However, regardless of the duration of the space flight or the form and amount of energy, and regardless of the structure of the water supply system, the use of any method under spaceflight conditions must satisfy the following equation: /45

$$\Sigma P_{supply} >> \Sigma P_{regeneration} \qquad 1.1$$

$$\Sigma(P_{wws} + P_{tank} + P_{p}) >> \Sigma(P_{equip} + P_{wm} + P_{energy} + P_{auto}), \qquad 1.2$$

where $P_{supply}$ is the weight of the system, based on the supplies; $P_{regeneration}$ is the weight of the system based on the regeneration processes; $P_{wws}$ is the weight of the water supply, oxygen or food; $P_{tank}$ is the weight of the tanks for storing water, oxygen or food; $P_p$ is the weight of the equipment or devices for prolonged storage of supplies (preservatives, refrigerators, etc.); $P_{equip}$ is the weight of the equipment in the regeneration devices; $P_{wm}$ is the weight of the waste materials (sorbents, catalysts, electrodes, mineral salts, etc.); $P_{energy}$ is the weight of the energy sources that make the regeneration process possible; $P_{auto}$ is the weight of the devices for automatic regulation of the regeneration systems.

Equations (1.1) and (2.1) indicate that the weight of the water supply system, based on regeneration processes, must be much less in comparison with the weight of systems based on supplies. However, even under the conditions

$$P_{supply} > P_{regeneration}$$

preference must be given to a system that is based on supplies, since the latter is characterized by maximum reliability and simplicity of operation. From this we obtain additional increases in the requirements placed on the reliability and the weight limitations of the regeneration systems, which in turn complicate the solution of problems involving the development of methods of water regeneration on space flights.

Sources of Water Subjected to Regeneration. Chemical Composition of Moisture-Containing Products of Human Vital Activity and Waste Products From Biological and Technical Systems

The sources of the water which is subjected to regeneration aboard a manned spacecraft can be moisture-containing products of the vital activity of man and animals, waste products from lower or higher plants, as well as the moisture given off by physical and chemical systems for supporting life.

As a result of human vital activity, moisture will enter the regeneration system as it is excreted by man with the sweat and from the lungs (the condensate of atmospheric moisture), as well as in the urine, feces, and water used for sanitary and hygienic purposes. In addition, regeneration will also make use of the water that is obtained as the result of washing dishes or in preparing food from the products of the greenhouse and higher heterotrophs. /46

Cultivation of lower and higher plants assumes the creation of contaminated solutions whose regeneration must provide man with drinking water and a stable functioning of biological systems. Such solutions include the moisture from transpiration of higher plants, the condensate from chlorella reactors, exhausted nutrient solutions from lower and higher plants, and solutions from the treatment of biomasses of chlorella.

The contaminated solutions that are formed as the result of the functioning of physical and chemical life support systems include the moisture given off by electrochemical current generators (fuel cells) and the water which is formed as the result of the catalytic hydration of carbon dioxide (according to the Sabatier reaction). In the event that the system for supplying oxygen and water to the crew of a spacecraft is designed on the basis of a utilization of the reaction involving the decomposition of hydrogen peroxide, regeneration will also involve the water formed as the result of catalytic decomposition of $H_2O_2$.

The quantity of moisture-containing products of human vital activity and waste products from biological and technical systems, calculated on the basis of one man-day, is shown in Table 4.

TABLE 4.* EXCRETION OF MOISTURE-CONTAINING PRODUCTS OF THE VITAL ACTIVITY OF A SINGLE HUMAN BEING AND THE FORMATION OF WASTE PRODUCTS FROM BIOLOGICAL AND TECHNICAL SYSTEMS

| Source of water used for regeneration | Amount of water, liters per day | Note |
|---|---|---|
| Condensate of atmospheric moisture | 1--2 | Up to 6-11 liters in extreme cases |
| Urine | 1—1,5 | Up to 8 liters in extreme cases |
| Feces | 0,1—0,3 | — |
| Water used for sanitation and hygienic purposes | 1,8--4 | Up to 25 liters on long flights |
| Water used for preparing food | 3 | — |
| Moisture from transpiration of higher plants | 85 | — |
| Exhausted nutrient solutions used for higher and lower plants | ... | The amount depends on the frequency with which the nutrient solutions are replaced |
| Condensate from chlorella reactors | 10 -15 | |
| Water from the indelible parts of higher plants | — | The amount depends on the method by which the water is extracted. |
| Solutions obtained in the processing of biomasses of chlorella | 7 | |
| Moisture given off by electrochemical current generators (fuel cells) | 11 | With a power of 1 kw |
| Water obtained in the Sabatier reaction: $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ | 0,8 | |
| Water obtained from the reaction: $H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$ | 0,9 | In obtaining 0.8 kg of $O_2$ |

*Note: Commas indicate decimal points.

A characteristic feature of moisture-containing waste products that are subjected to regeneration is a lack of constancy of their quantitative and qualitative ratios. Thus, for example, the daily amount of condensate of atmospheric moisture is an average of 1-2 liters per man. However, when the barometric pressure falls, under high temperature conditions and considerable physical and psychological stress, the amount of moisture excreted by man with the perspiration and from the lungs increases to 6-11 liters per day. Significant variations also can be seen in the daily diuresis of the cosmonauts: with an average level for daily diuresis of 1-1.5 liters, the amplitude of its variations can reach 0.5-8 liters of urine per day. The daily consumption of water used for sanitary and hygienic purposes (washing, showering, cleaning underclothing, etc.) can vary from 1.8 liters under the conditions of brief flights to 4 liters and even 25 liters a day per man on a long expedition (Oswald William et al., 1965; Rudek, 1967; Mendel, 1962). A certain degree of inconsistency in the quantitative relationships can be seen in the moisture from transpiration of higher plants, the condensate from chlorella cultivators as well as in exhausted nutrient solutions. The amount of contaminated water in these instances will be a function of the toxicity of the metabolites that have entered the culture solution, the nutrient solution and the condensate from the greenhouses or chlorella reactors, as well as the frequency with which the exhausted solutions are replaced. Maximum stability, quantitatively speaking, is evidently characteristic of the moisture given off by electrochemical power generators (fuel cells) as well as the water that is obtained as a result of hydration of carbon dioxide (Sabatier reaction) and the decomposition of hydrogen peroxide. /47

The sources of water used for regeneration are not limited to the list shown in Table 4. When new elements are included in the ecosystem, for example yeasts, hydrogenous bacteria, etc., new water sources will be available.

The choice of a method of water regeneration for spaceflight conditions is a function of the chemical composition of the products of human vital activity and the waste products from biological and technical systems, as well as the energy and weight limitations that apply to the specific spacecraft. In addition, considerable importance attaches to such spaceflight factors as the existence or absence of gravitation and the nature of the energy source. The relationship which exists between the method of water regeneration and flight duration or the number of crew members in the spacecraft is being overlooked. However, the chemical composition is one of the principal factors that govern the regeneration method. Let us examine the qualitative and quantitative composition of the solutions that are used for regeneration. The principal component of the *condensate* which is collected from the atmosphere of the cabin of the manned spacecraft is water (99.9%). Since the condensate of atmospheric moisture is composed of condensed water vapor in the system for purifying the air and regulating the temperature, its chemical composition will be determined by the concentration of gaseous and volatile compounds that are found in the atmospheres of manned spacecraft. /48

The atmosphere of a spacecraft cabin simulator in a 56-day experiment was found to contain 68 chemical compounds (Adams et al., 1966). Approximately 70 substances were found in 17-30 day experiments (Kee et al., 1963) in the

atmosphere of a Mercury spacecraft simulator. In these experiments the authors identified such compounds as methane, acetone, methyl, ethyl, propyl and butyl alcohol, formaldehyde, freons, skatole, propyl mercaptan and a number of other impurities.

The atmosphere (and consequently the condensate) contain substances excreted with the sweat and from the lungs of man. In addition, the condensate will be contaminated by volatile substances in the urine, feces, vomited materials, intestinal gases as well as technical contaminants such as compounds that are given off by the structural materials of the craft, paints, rubber and polymer materials, insulation, and products of the functioning of the life support systems.

The chemical composition of human sweat will depend upon the physical and psychological stresses placed upon the cosmonaut, his diet, individual characteristics of the organism and a number of other factors. It has been found that the sweat can contain such compounds as ammonia, urea, uric acid, creatinine, lipides, fatty acids, sodium chloride and many others. A number of the components of sweat are volatile. Some of the compounds, such as urea, undergo microbial decomposition to form ammonia and carbon dioxide, which also enter the condensate.

N. F. Tolkachevskaya (1940) gives the following composition (in %) for human sweat:

| | | | |
|---|---|---|---|
| Water | 97.7-99.6 | Urea | 124-161 mg % |
| Solids | 0.1-2 | Uric acid | 10 mg % |
| Mineral substances | 0.3-1.04 | Ammonium nitrate | 6-12 mg % |
| Carbon (total) | 0.2-0.4 | Acetic and formic acid, | |
| Lactic acid | 4-24 mg % | phenol, sulfuric acid esters, | |
| Creatinine | 3.5-5.0 mg % | aromatic hydroxy-acids. | + |

The air exhaled by man has been found to contain various chemical compounds which are produced by the vital activity of microorganisms in the oral cavity. Air exhaled by smokers is more polluted than air from nonsmokers (Gorban', 1964).

The number of volatile compounds that enter the condensate from the urine, feces, vomited material, etc. will depend on the effectiveness of the preservatives that are used to prevent microbial breakdown of waste products as well as the reliability of the system for storing them (Kustov, Tiunov, 1969). /49
Extremely diverse compounds will enter the condensate with technical impurities. Table 5 lists the products of the breakdown of certain materials that are used for equipment in spacecraft cabins under the influence of high temperatures (Clemedson, 1959).

At high temperatures and under conditions of reduced barometric pressure, the toxicity and volatility of a number of compounds in spacecraft cabins increase; some harmless substances begin to take on a toxic nature (Weber, 1963). /50
The considerable diversity and difference between the substances used, the equipment and processes for each individual spacecraft as well as the

differences in the parameters in the environment result in significant changes in the composition of the condensates of the atmospheric moisture.

TABLE 5. PRODUCTS GIVEN OFF BY VARIOUS MATERIALS IN THE CABINS OF SPACECRAFT UNDER THE INFLUENCE OF HIGH TEMPERATURES (Clemedson, 1959)

| Material | Products given off | Maximum permissible concentration in parts per million |
|---|---|---|
| Insulation, paint | carbon monoxide | 40 |
| | carbon dioxide | 5,000 |
| | halides | 0.1-1 |
| Plastics | carbon monoxide | 40 |
| | smoke | |
| | ozone | 0.1 |
| | halides | 0.1-1 |
| Resin | carbon dioxide | 5,000 |
| | aldehydes | |
| Cloth (natural, synthetic) | smoke | |
| | aldehydes | |
| Selenium rectifiers | selenium | |
| | hydrogen selenide | 0.05 |
| | selenium oxide | |
| | organic selenides | |
| Materials and substances contained in fire extinguishers: | | |
| carbon tetrachloride | | |
| | hydrogen chloride | 25 |
| | chlorine | 5 |
| | phosgene | 1 |
| | | 1 |
| chlorobromomethane | | 40 |
| | hydrogen bromide | 1 |
| | bromine | 1 |
| methyl bromide | | 20 |
| | carbonyl bromide | 0.5 |
| Machine oils | carbon monoxide | 40 |
| | carbon dioxide | 5,000 |
| | aldehydes | |
| | organic acids | |
| | oxidizers | |

Table 6 shows the chemical composition of the condensates of atmospheric moisture obtained aboard submarines, spacecraft cabin simulators, and a "Vostok" spacecraft. A characteristic feature of the chemical composition of these condensates is the extremely low concentration of mineral impurities. Such inorganic impurities as iron, titanium, chromium, aluminum, nickel, lead, /51 manganese and several others are found in trace amounts. In addition, the high acidity values indicate considerable pollution of the condensate by organic compounds. Judging by the considerable divergence in the acidity values determined on the basis of permanganate and bichromate methods, different

condensates contain a large number of compounds that are difficult to oxidize. In fact, the quantity of such substances which are difficult to oxidize as alcohols may be in excess of 2,500 mg/liter. It must be emphasized that the table lists only a small number of the compounds that were found in the condensate. Total listing of the chemical composition of the condensate of atmospheric moisture is a difficult problem.

TABLE 6. PHYSICAL CHARACTERISTICS AND CHEMICAL COMPOSITION OF THE CONDENSATES OF ATMOSPHERIC MOISTURE OBTAINED IN VARIOUS OBJECTS

| Factors | Spacecraft cabin simulator (Maseu et al., 1965) | Submarine (Wallman et al., 1965) | Pressurized chamber in an experiment lasting a year (Adamovich et al., 1971) | Cabin of a Vostok spacecraft |
|---|---|---|---|---|
| Oxidizability, $O_2$ mg/liter | | | | |
| bichromate | 450 | - | 60-160 | 144-240 |
| permanganate | - | - | 4-35 | 25-30 |
| Transparency, cm | Slightly cloudy, precipitate | - | 10 | Cloudy |
| Odor, degrees | Slight, unpleasant | 3 | 2-3 | 3 |
| Chromaticity, degrees | Colorless | 50 | - | - |
| pH | 7.1 | 2.5 | 7-8 | 6-6.9 |
| Suspended particles, mg/liter | 25 | 39 | - | - |
| Dissolved substances, mg/liter | 45 | - | - | - |
| Ammonia, mg/liter | Positive reaction | - | 8-90 | 70-160 |
| Chlorides, mg/liter | 0 | 1 | 8-54 | 3-22 |
| Sulfates, mg/liter | 0 | - | - | 3-5 |
| Nitrates, mg/liter | - | - | 0.2 | 0.6-1 |
| Hardness, mg·eq/liter | - | - | - | 0.2-0.3 |
| Calcium, mg·eq/liter | - | 0.05 | 0-72 | 4-29 |
| Iron, titanium, chromium, aluminum, nickel, lead, manganese, mg/liter | - | 0.7-7 | - | - |
| Alcohols, mg/liter | - | - | 0-10 | 330-2500 |
| Aldehydes, mg/liter | - | - | 0.9 | - |
| Acids (carbonic), mg/liter | - | - | 10-15 | 15-27 |
| Bacterial contamination, microbes/ml | Considerable | $1 \cdot 10^5$ | $10^5$ | - |
| Coli titer, microbes/500 ml | 15 | - | - | - |

In terms of its chemical composition, urine is one of the most polluted sources of the water that is to be used for regeneration. It is a complex aqueous solution of a great many chemical compounds, both organic and inorganic. The total amount of water in the urine can reach 95%. The composition of the solid residue which makes up about 5% includes a number of chemical compounds: electrolytes and nitrogenous substances, as well as the products of metabolism and the breakdown of tissues, hormones, enzymes and a number of other metabolites. It has been established that human urine contains up to 200 different

compounds (Tolkachevskaya, 1940; Saretskay, 1963; Puenescu, 1963; Zbarskiy et al., 1954; Gulevich, 1945; Naidov, 1969). According to the data from other authors (Putnam, 1965) who used the method of chromatographic analysis, urine contains more than 140 chemical compounds. Table 7 is a chemical analysis of the composition of urine.

TABLE 7. CHEMICAL COMPOSITION OF THE DAILY URINE IN MAN ACCORDING TO THE DATA OF VARIOUS AUTHORS (in mg)

| Chemical compounds | Tolkachevskaya (1940) | Gulevich (1945) | Mangelsdorf (1959) |
|---|---|---|---|
| Water | 95% | 95% | 95% |
| Urea | 20 000—35 000 | 20 000—30 000 | 30 000 |
| Sodium chloride | 8 000—18 000 | — | 12 000 |
| Creatinine | 500—2 400 | 600—2 000 | 1 200 |
| Phosphorus ($PO_4$) | 2 000—13 000 | — | — |
| Ammonia | 400—1 200 | 500—1 100 | — |
| Hippuric acid | 100—2 500 | — | 700 |
| Uric acid | 200—1 200 | 300—1 200 | 700 |
| Sodium | 4 000—9 000 | — | 4 000 |
| Potassium | 2 000—3 300 | — | 2 000 |
| Calcium | 200—970 | — | 200 |
| Magnesium | 60—200 | — | 150 |
| Sulfur | 1 800—3 600 (as $SO_4$) | — | 2 500 (as S) |
| Inorganic sulfates | 1 210—3 030 | — | 2 000 (as $SO_3$) |
| Neutral sulfur | 200 | — | 300 (as $SO_3$) |
| Oxalic acid | 15—30 | — | 20 |
| Nitrogen from amino acids | 180—530 | — | 200 |
| Purinic bases | 15—45 | — | 10 |
| Phenols | 17—420 | — | 200 |
| Volatile fatty acids | up to 60 | — | — |
| Citric acid | 200—1 000 | — | — |

It follows from the table that 80% of the impurities are found in the first 10 components. The composition of urine can be divided into two groups of compounds: mineral substances and impurities of an organic nature. Among the mineral compounds, the most important is sodium chloride, whose daily amount changes from 8-12 grams. The amount of potassium varies from 2 to 3.3 grams while the sulfates that are formed from amino acids that contain sulfate vary from 1.5 to 3.7 grams. Of the substances of an organic nature, the most important are the nitrogenous compounds. Thus, the daily amount of urea excreted with the urine varies from 20 to 35 grams; for creatinine the figure is 0.5 to 2.4 grams, for uric acid 0.2 to 1.2 grams; hippuric acid, 0.1 to 2.5 grams, and ammonia 0.4 to 1.2 grams. In addition, the products of

incomplete oxidation of proteins are excreted with the urine -- amino acids such as lysine, arginine, histidine, treoline, aspartic and glutaminic acid, ericine, etc.

The change in the pH of the medium is very important in the development of water regeneration methods. As a rule, fresh urine yields a slightly acid reaction, although variations in the pH from 4.5 to 8.4 have been observed (Tolkachevskaya, 1940; Gulevich, 1945). These variations in the pH are caused by alkaline fermentation of the urine, involving the breakdown of urea to form ammonium carbonate under the influence of microorganisms and the enzyme urease, /52 according to the following equations:

$$(NH_2)_2CO \xrightarrow{+2H_2O} CO(ONH_4)_2$$

$$CO(ONH_4)_2 \longrightarrow 2NH_3 + CO_2 + H_2O.$$

Ammonium carbonate shifts the pH toward the alkaline, leading to the formation and settling out as a precipitate of the phosphate salts of calcium and magnesium: $Ca_3(PO_4)_2$, $Mg_3(PO_4)_2$, $MgNH_4PO_4$. In addition, the precipitate may contain uric acid, its salts (urates), acid calcium phosphate ($CaHPO_4$) and a number of other compounds. Under the influence of spaceflight factors, the amount of salts excreted with the urine may change. It has been noted that when man is exposed to orbital flight conditions there is an increased excretion from the organism of such elements as calcium, phosphorus, magnesium, potassium, and sodium (Calloway, 1964; Biryukov et al., 1967).

In addition to the compounds listed above, the urine may also contain /53 physiologically active substances -- hormones or products of their decomposition. Urine has been found to contain from 7 to 35 mg/liter of corticosteroids, and up to 15 mg/liter of aldosterone. It should be noted that all physiologically active substances that are excreted with the urine are thermally unstable compounds.

In developing water supply systems based on regeneration processes, it is necessary to take into account that urine contains volatile and gaseous compounds such as $CO_2$, methyl sulfates, alcohols, etc.

Another potential source of water is the feces, whose chemical composition is listed on the next page./

As we can see from these data, the amount of water in the feces is small and amounts to 65-280 grams per day per man. In view of the unusual diversity and considerable concentrations of chemical, biochemical and microbiological components in the feces, as well as a comparatively small amount of water, the necessity of separating it from the feces and purifying it is problematical, particularly on short space flights.

CHEMICAL COMPOSITION OF FECES (Zbarskiy et al., 1954; Tolkachevskaya, 1940)

| Component | Daily Amount |
|---|---|
| Feces | 100-330 grams |
| Dry residue | 10-25% |
| Water | 65-85% |
| Ash of dry residue | 11-16% |
| Soap as fatty acids | 2.6-4.7% |
| Fat (as stearic acid) | 11-13% of the dry residue |
| Starch (as glucose) | 0.6-13.5% of the dry residue |
| Free fatty acids | 0.2-1.5% of the dry residue |
| Bound fatty acids | 6.9% of the dry residue |
| Volatile fatty acids | 0.65% of the dry residue |
| Acetic and oleic acids | 30-60% of the total amount of volatile fatty acids |
| Organic acids (others) | 1 gram |
| Indole | 4.0-5.0 mg |
| Urobilin | 50-230 mg |
| Nitrogen (total) | 1.5-7% of the dry residue |
| Potassium | 10% of the dry residue |
| Sodium | 2.3% of the dry residue |
| Ammonia | 0.2-0.16% of the dry residue |
| Calcium | 20.8% of the dry residue |
| Sulfur | 0.8% of the dry residue |
| Phosphates | 18.4% of the dry residue |
| Microflora | 8% of the dry residue |

Beginning with flights of moderate duration, regeneration must involve the use of water used for sanitary and hygienic purposes as well as for cooking. /54 The composition of water used for sanitary and hygienic purposes will be determined by the nature of the substances used for washing, the frequency of the hygienic procedures, the schedule for work and rest of the cosmonauts, the food ration and several other factors involved in space flight. The chemical composition of the water used for sanitary and hygienic purposes is shown in Table 8.

A characteristic feature of water used for sanitary and hygienic purposes is the inclusion of a considerable amount of fat in its composition. In addition, water used for sanitary and hygienic purposes shows high levels of microbial contamination.

The chemical composition of cooking water is basically determined by the food ration of the cosmonauts. The following are some of the parameters in the composition of cooking water:

| | | | |
|---|---|---|---|
| Dry residue, mg/liter | 6,000-7,500 | Nitrogen, ammonium, mg/liter | 5-50 |
| Fats, mg/liter | 600-2,000 | Nitrogen, nitrite, mg/liter | 5-13 |
| Oxidizability, $O_2$ mg/liter | | | |
| permanganate | 1,200 | pH | 5-7.5 |
| bichromate | 7,900-8,700 | Chlorides, mg/liter | 150 |

TABLE 8. PHYSICAL CHARACTERISTICS AND CHEMICAL COMPOSITION OF WATER USED FOR SANITARY AND HYGIENIC PURPOSES ACCORDING TO THE DATA OF VARIOUS AUTHORS

| Components | Wallman et al., (1965) | Hansen, Berger (1965) | Adamovich et al., (1971) |
|---|---|---|---|
| Chromaticity, degrees | greyish | colorless | grey |
| Odor, degrees | typical | unpleasant | sharp specific |
| Transparency, cm | cloudy | cloudy residue | cloudy |
| pH | 4.8 | 7.1 | 6-7 |
| Oxidizability, $O_2$ mg/liter | | | |
| permanganate | — | 450 | 600 |
| bichromate | — | — | up to 5,000 |
| Nitrogen, $NH_3$, mg/liter | — | — | 60 |
| Urea, mg/liter | 100 | — | 3 |
| Nitrogen from nitrites, mg/liter | — | — | 0.25 |
| Sulfur ($SO_4$), mg/liter | negative reaction | negative reaction | 40 |
| Chlorides, mg/liter | 240 | negative reaction | 300 |
| Calcium, mg/liter | — | — | traces |
| Magnesium, mg/liter | — | — | traces |
| Fats, mg/liter | 180 | — | 800 |
| Soluble substances, mg/liter | 550 | 45 | — |
| Insoluble substances, mg/liter | 1,000 | 25 | — |
| Microbial population, microbes/ml | — | considerable | 120,000 |

Cooking water contains considerable amounts of suspended matter (up to 7,000 mg/liter). It must be kept in mind that cooking water constitutes a suspension and a solution of nutrient components. Since it constitutes an excellent medium for the multiplication of microorganisms, cooking water may change its chemical composition markedly in the course of storage or processing. /55

Long space flights assume the possibility of using the elements of higher and lower plants in life support systems for the crew. In this case, the regeneration will involve water of transpiration, condensed from the atmosphere of the greenhouse and the chlorella cultivator, as well as exhausted nutrient solutions. Water transpiration includes volatile soluble compounds excreted by the plants as well as impurities whose nature and concentration depend upon the structural materials of the greenhouse. Nutrient solutions that have been exhausted will contain some of the mineral components not used by the plants as well as organic compounds (metabolites) excreted by the plants in the course

of their cultivation. A sample of the composition of water transpiration can be found in Table 9.

TABLE 9.* EXAMPLE OF CHEMICAL COMPOSITION (in mg/liter) OF A CONDENSATE OF WATER TRANSPIRATION FROM HIGHER PLANTS

| Plant | Oxidizability, $O_2$ mg/liter: permanganate | Oxidizability, $O_2$ mg/liter: bichromate | Total hardness, mg·eq/liter | pH | $NH_3$ | $NO_2^-$ | $NO_3^-$ | $Cl^-$ | $SO_4^{-2}$ | $Ca^{+2}$ | $Mg^{+2}$ | $Cu^{+2}$ | $K^+$ | $Na^+$ | $Mn^{+4}$, $Fe^{+2}$, $Fe^{+3}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Beets | 8 | 14 | 0,95 | 6,0 | 0,5 | 0,03 | 0,02 | 8 | 35 | 14 | 20 | 0,9 | 0 | 0 | 0 |
| Carrots | 10 | 24 | 0,8 | 3,5 | 0,6 | 0,02 | 0,1 | 3 | 41 | След | 8,5 | 1,1 | 0 | 0 | 0 |
| Cabbage | 5 | 16 | След | 5,0 | 53 | 0,03 | 0,1 | 17 | 20 | 0,5 | 0,8 | 0,7 | 0 | 0 | 0 |
| Radishes | 12 | 37 | 0,4 | 5,0 | 0,6 | 0,5 | 0,8 | 3 | 89 | 3 | 1,5 | 0 | 0 | 0 | 0 |
| Potatoes | 9 | 87 | 0,2 | 8 | 8 | 0,16 | 0,5 | 3 | 24 | 1,4 | 2,6 | 0 | 26 | 60 | 0 |

*Note: Commas indicate decimal points.

It follows from the table that the amount of impurities in the water of transpiration is small. The total amount of organic impurities determined by the permanganate and bichromate methods changes from 9 to 12 and from 14 to 87 $O_2$ mg/liter, respectively. There are practically no inorganic compounds. The exhausted nutrient solutions from lower and higher plants contain considerable quantities of unbound mineral salts.

The chemical composition of urine-fecal solutions, mineralized by the microbiological method, indicates that in addition to the organic and mineral impurities, the microorganisms (whose numbers can reach significant levels) are removed as well (Tsitovich et al., 1967).

The moisture given off by technical systems includes solutions that are /56
obtained as a result of the functioning of electrochemical current generators (fuel cells), reactors for decomposition of hydrogen peroxide and reactors used for the hydration of carbon dioxide (according to the Sabatier reaction).

The principal types of electrochemical generators are hydrogen-oxygen fuel cells with potassium electrolyte and ion-exchange membranes (Yusti, Vinzel', 1964). The chemical composition of the moisture given off by the fuel cells is shown in Table 10.

It follows from the table that potassium hydroxide is the principal component in the moisture given off from fuel cells that use potassium electrolyte. The principal impurities in the moisture given off by fuel cells with ion exchange membranes are the organic compounds.

It should be kept in mind that American researchers have attempted to make animals (monkeys) drink the moisture given off from the fuel cells without purifying it or subjecting it to subsequent conditioning. In some individuals,

intestinal ailments were observed. Aboard the "Gemini-5" spacecraft, whose flight lasted 8 days, the water given off from the fuel cells was used for drinking purposes by two astronauts. However, in later studies (Sauer, Shea, 1969), on the basis of the results of the flight of the "Gemini-8" spacecraft and the "Apollo" it was pointed out that the water from fuel cells is characterized by negative organoleptic properties.

TABLE 10.* CHEMICAL COMPOSITION OF MOISTURE GIVEN OFF BY FUEL CELLS

| Impurities | Fuel Cells | |
|---|---|---|
| | With potassium electrolyte | With ion exchange membranes |
| KOH, mg/liter | 10–100 | |
| pH | 9 | 5–6 |
| Oxidizability, $O_2$ mg/liter | | |
| bichromate | 50–300 | 60–280 |
| permanganate | 7–100 | 5–60 |
| Odor, degrees | 0 | 2 |
| Transparency, cm | 10–15 | 30 |
| Methanol, mg/liter | 0,1–10 | 1,6 |
| Ethanol, mg/liter | 0,2–8 | 7–13 |
| Ammonia, mg/liter | 0,5–20 | 1–13 |
| Acetic acid, mg/liter | 0,1–50 | 30–90 |
| Oleic acid, mg/liter | 3,5 | 1–45 |
| Hardness, mg·eq/liter | Traces | 0.7 |

*Note: Commas indicate decimal points.

Water supply systems can use water which is obtained as the result of the decomposition of hydrogen peroxide. In fact, one kg of 92% hydrogen peroxide will yield 0.43 kg of oxygen and 0.57 kg of water, giving off about 600 kcal of heat. /57

Screens made of activated silver or steel screens covered with silver are used as a catalyst to decompose the hydrogen peroxide; they operate at a temperature of 120-700°. However, the water which is obtained from hydrogen peroxide cannot be used directly without purifying it. This is because $NaSnO_3$, $Na_4P_2O_7$ and $NH_4NO_3$ are used for stabilization of the highly concentrated hydrogen peroxide and for preventing corrosion of the containers and pipes. As a result of the decomposition, these substances enter the condensate and make it possible to use for drinking purposes. The condensates have been found to contain large quantities of tin, phosphates and silver.

Water obtained as a result of hydration of $CO_2$ (Sabatier reaction) is characterized by a comparatively high degree of purity. In this case the impurities are due primarily to structural materials in the catalytic reactors that operate under high temperature conditions (approximately 300°).

From the above survey it follows that the products of human vital activity which contain moisture and the waste products from biological-technical systems are characterized by extremely diverse impurities that must be removed. Considerable differences in the nature of the impurities and their quantities make it necessary to develop various ways of regenerating water which will satisfy the conditions aboard a specific spacecraft.

## Classification of Impurities That Enter the Composition of Products of Human Vital Activity and Waste Products from Biological and Technical Systems

Various substances and compounds, which differ as to amount, total composition and chemical nature, enter the composition of moisture-containing products of human vital activity and biological and technical systems.

In order to facilitate the search for physical-chemical methods of water regeneration, it is advisable to classify all of the impurities on the basis of some characteristic. On the basis of the work of L. A. Kul-skiy (1968), who worked out one of the classification systems for impurities that form part of natural water, all impurities can be classified which can be removed from waste products on the basis of the size of their particles, for example. On the basis of this criterion, all impurities can be divided into six groups (Table 11):

dissolved solids;
liquid compounds;
volatile and gaseous impurities;
colloidal compounds;
microorganisms;
coarsely dispersed suspended particles.

TABLE 11. CLASSIFICATION OF IMPURITIES ON THE BASIS OF PARTICLE SIZE /58

| Group | Particle size, cm | Impurities | Waste products in which they are contained |
|---|---|---|---|
| 1. Dissolved solids | $10^{-7}$-$10^{-8}$ | NaCl, $(NH_2)_2CO$, KOH, $NH_4OH$, $(NH_4)_2CO_3$, etc. | In the urine, moisture given off by electrochemical automatic gas analyzer, condensate of atmospheric moisture, nutrient solutions from plants. |
| 2. Liquid compounds | $10^{-6}$-$10^{-7}$ | Aldehydes, alcohols, ketones, acids, etc. | In the condensate of atmospheric moisture, urine, etc. |
| 3. Volatile and gaseous impurities | $10^{-6}$-$10^{-7}$ | Hydrogen, ethers containing sulfur, ammonia, carbon dioxide, aldehydes, alcohols, etc. | In moisture given off by electrochemical automatic gas analyzers, urine, condensate of atmospheric moisture, in solutions from physical-chemical and biological mineralization. |
| 4. Colloidal compounds | $10^{-5}$-$10^{-6}$ | Soaps, mucoids, etc. | In water used for sanitary and hygienic purposes, urine. |
| 5. Microorganisms | | E. coli, etc. | In practically all waste products containing moisture. |
| 6. Coarsely dispersed suspended particles | More than $10^{-4}$ | Cells of water plants (for example, chlorella), epithelial cells, activated sludge, residues of $CaCO_3$, $Ca_3(PO_4)_2$, cellulose, etc. | In the nutrient fluid of unicellular algae, in the urine, water used as sanitary and hygienic purposes, solutions of physical-chemical and biological mineralization, feces. |

Under terrestrial conditions, various methods employed in the practice of water treatment and supply can be used to remove impurities (Kul'skiy, 1961, 1963, 1968; Kastal'skiy, Mints, 1962; Apel'tsin, Klyachko, 1968). Thus, various types of distilling apparatus are used to remove pollutants of the first group, as well as electrodialysis, ion exchange, and membrane processes.

Freeing water of impurities of the second group can be accomplished by rectification, the microbiological method and sorption.

Extraction of pollutants of the third group is possible by means of aeration, ozonization, chlorination or sorption.

Compounds of the fourth group may be eliminated by filtration of the precipitate which is obtained following coagulation and precipitation.

Following the stage of decontamination, microorganisms can be removed by filtration through bacterial filters or by means of coagulants. Coarsely dispersed suspended substances, which make up the sixth group, are easily removed by precipitation and filtration.

Under spaceflight conditions, considerable corrections to this classification system are made by such parameters as the concentration of the impurities. In fact, such slightly concentrated solutions as the condensate of atmospheric moisture, the moisture which is given off by fuel cells, the water of transpiration of higher plants and certain others can be purified by the sorption method. It is not a good idea to use such methods as evaporation or distillation for these purposes because of the considerable energy losses. The /59
latter methods can be used to extract water from such concentrated solutions as urine, as well as the water that is used for sanitary and hygienic purposes or cooking. It is also advisable to use such methods as reverse osmosis, evaporation through a membrane, electrodialysis, etc.

On the basis of the colloidal properties of the impurities in the solutions of the fourth group, it is a good idea to use coagulation with subsequent filtration or centrifuging for regeneration of the water. In order to purify the water and remove impurities of the fifth group it is necessary to use effective methods of decontamination in view of the fact that the waste products of vital activity constitute a good medium for the rapid multiplication of microorganisms. Impurities of the sixth group may be eliminated by means of centrifuging or filtration.

Methods of Preliminary Processing of Waste Products

The moisture-containing products of human vital activity and waste products from biological systems constitute a favorable medium for the growth of various microorganisms.

Despite the fact that excreted moisture such as fresh urine is sterile (Gulevich, 1945), there is a possibility that it will be contaminated by various putrefactive and fermentative microorganisms when it is collected and stored. This probability increases with increasing length of the tubing

connecting the source of the moisture which is given off and the system for water regeneration. In addition, many methods for water regeneration operate at room temperature: this also promotes multiplication of microorganisms in waste products. During the vital activity of microorganisms, there is a breakdown of the organic and inorganic components with formation of new classes of compounds. Thus, the alkaline fermentation of urine gives it its sharp odor of ammonia, due to the vital activity of urobacteria as well as vulgar putrefactive bacteria (Proteus vulgaris), which are responsible for the process of the decomposition of the urea in urine to form ammonia and carbon dioxide. The ammonia which is given off changes the pH to the alkaline side, leading to precipitation of salts of calcium, magnesium, etc. The fermentative processes can lead to the formation of various volatile compounds in the urine, for example, acetic and oleic acid, etc. As a result of the vital activity of intestinal bacilli in the urine, hydrogen sulfide will develop.

Changes in the chemical and aggregate composition of waste products as a result of vital activity of microorganisms may have a significant influence on the technological parameters of water regeneration processes. For example, the precipitation of sediments is associated with the plugging of membranes, evaporators, valves, pumps, phase separators, etc. The liberation of volatile compounds makes it necessary to use additional purification elements. Insoluble or slightly soluble gases will cover the surfaces of ion-exchange resins or activated charcoal, thereby lowering the exchange and sorption capacity of the layer. The formation of a gas phase leads to a breakdown of /60
the continuity of the hydraulic curve and the increase in hydraulic resistance. Therefore, before the moisture-containing products of vital activity enter the water regeneration system, they must be subjected to preliminary treatment in order to prevent microbiological processes from occurring. Regardless of the microbiological pathway for generation of a volatile compound, the latter will be present in various moist secretions, and will be a component of them. Thus, water used for sanitary and hygienic purposes and urine contain free ammonia, acids and a number of other volatile impurities. In order to ensure the more reliable operation of regeneration systems it is advantageous to bind such substances with thermostable compounds. Therefore, preliminary processing must include these operations. Ammonia may be bound by means of various chemical reagents. The best one for this purpose is sulfuric acid (Table 12).

Volatile substances may be oxidized in the presence of these or other oxidizers or they may be removed by means of activated charcoal. The chemical composition of the products of vital activity may change during their storage as a result of chemical reactions, for example hydrolysis. The temperature factor and the nature of the structural materials of which the regeneration system is composed are very important in this regard. In the latter case, several metals make active catalysts, accelerating the chemical reactions with /61
formation of undesirable products. Hence, the assembly for preliminary processing must ensure a binding of ammonia, oxidation or sorption of volatile compounds and decontamination of the products of vital activity. It is obvious, however, that the greatest danger is posed by the microbiological pathway for transformation of the products of vital activity and the main problem in the preliminary processing of the wastes is bound to be their decontamination.

TABLE 12.* CHARACTERISTICS OF CERTAIN AMMONIUM SALTS

| Ammonium salt | Molecular weight | Temperature of decomposition or sublimation of the anhydrous salt |
|---|---|---|
| Acetate, $NH_4C_2H_3O_2$ | 77,1 | 237 |
| Bromide, $NH_4Br$ | 98,0 | 1008 |
| Carbonate, $(NH_4)_2CO_3$ | 96,1 | 136 |
| Bicarbonate, $NH_4HCO_3$ | 79,1 | 97—140 |
| Chloride, $NH_4Cl$ | 53,5 | 662 |
| Chromate $(NH_4)_2CrO_4$ | 152,1 | 356 |
| Bichromate, $(NH_4)_2Cr_2O_7$ | 252,1 | Decomposes |
| Formiate, $HCO_2NH_4$ | 63,1 | 356 |
| Nitrate, $NH_4NO_3$ | 80,1 | 410 |
| Persulfate, $(NH_4)_2S_2O_8$ | 228,2 | 248 |
| Diorthophosphate, $NH_4H_2PO_7$ | 115,0 | Does not break down in a boiling aqueous solution at 1 atm |
| Hypophosphate, $NH_4H_2PO_2$ | 83,0 | 464 |
| Sulfate, $(NH_4)_2SO_4$ | 132,2 | 955 |
| Bisulfate, $NH_4HSO_4$ | 115,1 | 914 |
| Rhodanide, $NH_4CNS$ | 76,1 | 338 |

*Note: Commas indicate decimal points.

Decontamination of the products of human vital activity and the waste products of biological systems may be accomplished by physical, biological or chemical means. The physical methods include the action of high temperatures, ultraviolet radiation, treatment with ultrasound, action of ionizing radiation, and treatment with a magnetic field. Several of these methods of decontamination are discussed in Chapters II and IV. However, the decontamination of moisture-containing products of vital activity for the purpose of subsequently extracting water from them poses distinctive problems. Thus, for example, it is not a good idea to use heat treatment of urine, inasmuch as decomposition of urea and other thermolabile compounds takes place, forming volatile gaseous molecules.

The use of ultraviolet radiation is not very effective, since the suspended, colloidal and other impurities prevent the penetration of the ultraviolet into the depths of the water, scattering or absorbing it in the thin surface layer. Decontamination of waste products by means of ultrasound involves considerable energy expenditure. It is difficult to carry out decontamination by the radiation method because of the need to use heavy shielding against ionizing radiation.

These methods of decontamination have a common shortcoming: their lack of an aftereffect. After the waste products have been treated by these methods, any microorganism that should chance to penetrate would be even more able to develop and to change the chemical composition of the medium, since there would be no microbial antagonists. The processes of microbial antagonism may be used in a biological method for processing the wastes. However in this case various gaseous compounds will also be given off. Evidently, the best solution to the problem of decontamination of waste products is the chemical method.

Under spaceflight conditions, V. V. Borshchenko et al., (1970) studied the antiseptic properties of such chemical reagents as silver nitrate, copper sulfate, hexachlorophene, and paranitrophenol. They showed that the use of paranitrophenol at a concentration of 5 g/liter inhibited the growth of microorganisms during the 30 days that urine was stored in a waste-disposal device in a container for animals during the flight of the "Cosmos-110" artificial Earth satellite. It is difficult to use paranitrophenol to decontaminate waste products that enter the regeneration system because of the difficulty of identifying and removing it from the water after it has been regenerated. /62

Chlorine is a widely used antiseptic. Dissolved in water, chlorine forms hydrochloric and hypochlorous acid. The latter can produce chloramines with the ammonia in urine:

$$NH_3 + HClO \longrightarrow NH_2Cl + H_2O$$

$$NH_3 + 2HClO \longrightarrow NHCl_2 + 2H_2O$$

$$NH_3 + 3HClO \longrightarrow NCl_3 + 3H_2O$$

However, it is not a good idea to use chlorine in water regneration systems because of its volatility, toxicity and corrosive action. Extensive studies of the use of the chemical method of decontamination were performed by Putnam (1965). Table 13 shows the effectiveness of several antiseptics which he used for the preservation of urine.

TABLE 13. RELATIVE EFFECTIVENESS OF SEVERAL ANTISEPTICS (Putnam, 1965)

| Antiseptic | Time of Sterility of Urine |
|---|---|
| Ions of heavy metals: Cu, Fe, Ag, Co, Hg, etc. | From 2 to 9 months as a function of the metal concentration. |
| Oxidizers: $CrO_3$, $H_2O_2$, HOCl, NaOCl, $LiNO_3$, $KMnO_4$, $HClO_4$, $Ca(ClO)_2 \cdot 4H_2O$, etc. | From 2 days to 2 weeks. |
| pH = 11 | More than 6 weeks. |
| pH = 2 | More than 6 weeks. |

If urine, containing up to 600 mg/liter of ammonia, is treated with copper sulfate with a concentration of 5 g/liter, the evaporation of the urine will yield a condensate which contains 0.25 to 20 mg/liter of ammonia. Increased quantities of ammonia are observed only in cases of an intensive process of extraction of water from the urine. In the case of treatment with copper

sulfate (5 g/liter) and hydrogen peroxide (2 g/liter of a 3% solution of $H_2O_2$) the urine can be stored without decomposing for 9 months. The major shortcoming of these antiseptics is the formation of precipitates that settle out and plug tubing and assemblies in the regeneration system. A very promising approach is the use of chromium oxide which forms ammonium chromate with ammonia and is capable of oxidizing a number of organic compounds (Putnam, 1965). However, the transition of hexavalent chromium to the trivalent state involves the settling out of a precipitate -- the hydroxide of trivalent chromium. The best solution is to use a mixture of $CrO_3$ and $H_2SO_4$. Sulfuric /63 acid binds the free ammonia to form heat-resistant ammonium sulfate. Chromium oxide oxidizes the volatile substances and acts as an antiseptic. However, chromium oxide is difficult to dissolve in sulfuric acid. Therefore, Putnam recommends that the chromium oxide be dissolved first in water and then in acid. As a result, a solution is formed which consists of 44.7% sulfuric acid, 44.3% water and 11.0% chromium oxide. The specific gravity of the resultant solution is 1.44, so that 3.6 ml of the solution must be used per liter of urine.

Special emphasis must be placed on the fact that this mixture is the best one for this method of regeneration of water (in the specific case, for evaporation or distillation). If other methods of regeneration are used, this preservative may prove unsuitable. For example, when storing water used for sanitary and hygienic purposes, chromium oxide and sulfuric acid can change the technological conditions for coagulation by shifting the pH to the acid side. It is difficult to use this mixture for decontamination of water of transpiration from lower and higher plants, where it would be more effective to use a different approach to the choice of the preservative for individual sources of polluted water and methods of purifying them. In addition, the selected preservative must not exhibit a high level of toxicity or corrosivity and must be eliminated easily from the water regeneration system. Unfortunately, the literature contains very little on the preservation of products of human vital activity and waste products from biological and technical systems as they apply to problems of water regeneration under conditions of limited closed areas.

The Sorption Method of Water Regeneration

The choice of a sorbent, in particular, depends on the nature of the chemical impurities that are to be removed. As we pointed out earlier, the moisture-containing products of human vital activity and those from biological and technical systems include electrolytes and compounds of a non-ionic nature. In order to eliminate the electrolytes, it is a good idea to use ion-exchange resins; substances of a non-ionic nature may be removed by various molecular sorbents, mainly activated charcoal.

The extraction of impurities by the ionite method can be accomplished either by filtering the solution through a layer of ion-exchange resins (the dynamic method) or by processing the polluted water with a certain amount of ionite (the static method). Under spaceflight conditions, the dynamic version is best.

Ionites are solid, practically insoluble materials that are capable of ion exchange. Natural mineral ionites are known (apatites, zeolites), but there are also natural ionites of organic origin (humic acids in soil) and artificial ionites -- ion-exchange resins. The first three types of ionites are characterized either by low exchange capacity or weak chemical and mechanical strength. The ones that have been found to be most suitable for use in water purification are the synthetic ion-exchange resins (Saldadze, Pashkov, Titov, 1960; Griessbach, 1957; Gel'ferich, 1962). At the present time, a number of sorbents have been synthesized which possess different properties. Their use for the regeneration of water under spaceflight conditions will depend primarily upon the nature of the impurities to be removed. Thus, for example, alkali forms part of some of the moisture-containing waste products from fuel cells. To extract it, it is desirable to use such cationites as KU-1, KU-2, SDV-3, KB-4, RF and several others. /64

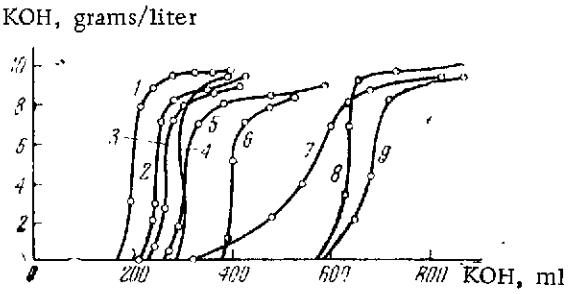


Figure 2. Output Curves for Alkali; Passage of a 1% Solution of KOH Through Cationites of Various Types. 1, KU-5G; 2, SDV-3; 3, KU-2X8; 4, KU-2X20; 5, KU-1; 6, RF; 7, KB-4V; 8, KB-4P2; 9, KB-4X25.

The results of the studies performed by these authors showed that the greatest exchange capacity is possessed by the KB-4 carboxyl-containing cationites and RF which contains phosphorus. Figure 2 shows data on the sorption of alkali from 1% solutions of KOH in the presence of various cationites. The results were obtained by means of the device shown in Figure 3. However, the maximum capacity per unit weight of absolutely dry cationite is still not an absolute criterion of suitability of this substance for water regeneration systems. The degree of swelling of the resin is important in this regard. In the following table we have listed the values for swelling (in %) for various cationites in water and in an alkaline solution. These data indicate that the KB-4 cationites swell to the greatest extent.

| Cationite | In Water | In a 1% Solution of KOH | Cationite | In Water | In a 1% solution of KOH |
|---|---|---|---|---|---|
| KU-2X20 | 60 | 65 | KU-1 | 110 | 135 |
| RF | 90 | 80 | KB-4B | - | 210 |
| KU-2X8 | 105 | 102 | KB-4X25 | 80 | 240 |
| KU-5G | 190 | 108 | KB-4P2 | 80 | 250 |
| SDV-3 | 165 | 130 | | | |

/65

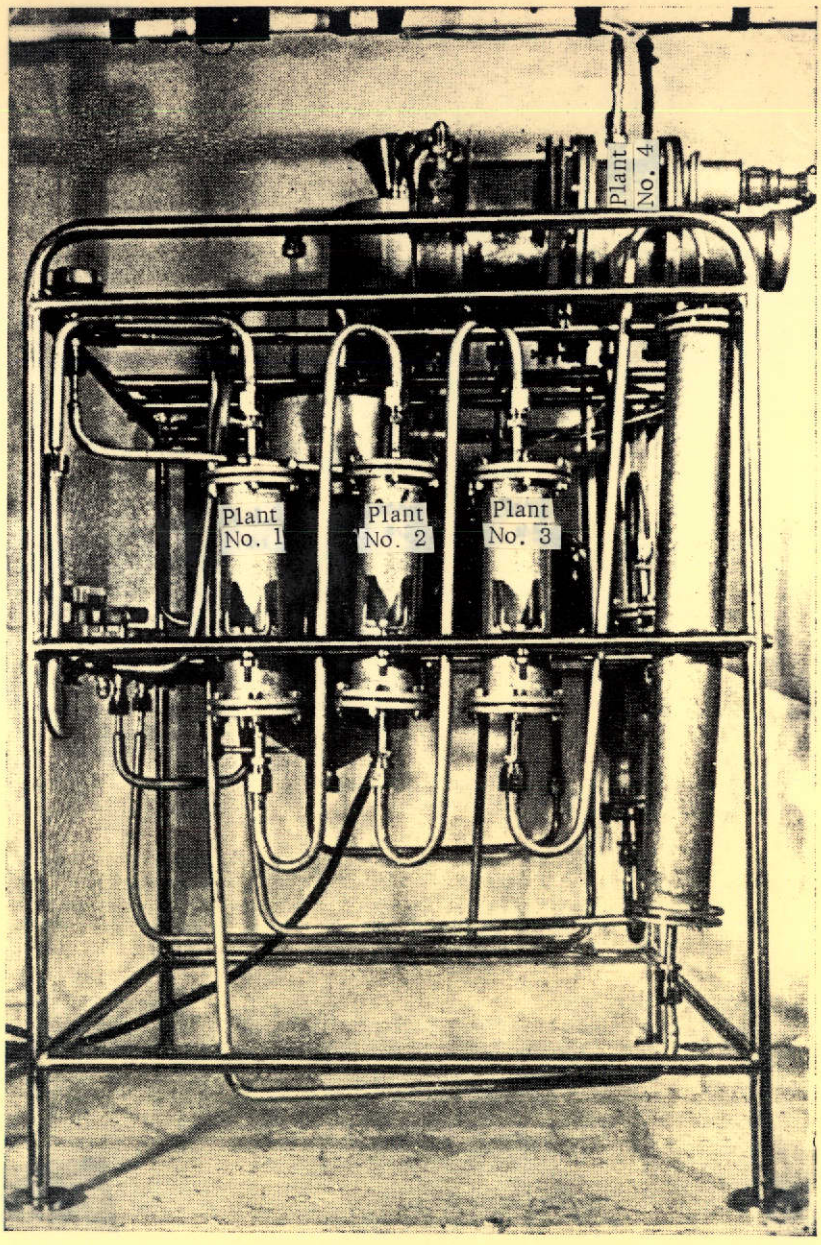


Figure 3. External View of a Laboratory Device For Regenerating Water By The Sorption Method.

/66

An increase in the degree of swelling causes an increase in the volume of the regeneration system and an increase in the resistance to the flow of the solution being cleaned. Therefore, preference must be given to type KU-2 cationite. In turn, the degree to which KU-2 cationite swells has to do with the quantity of "linking" agent (divinylbenzene) in the resin. V. V. Shaydorova and M. I. Salikova (1969), studying the exchange capacity of KU-2 cationite

with a divinylbenzene content of 8, 12, 16, 20 and 26%, showed that KU-2 strongly bound cationites can reduce the sorbent weight by 15 to 19% in comparison with KU-2 which contains 8% divinylbenzene when purifying water to remove alkali.

In contrast to the moisture obtained from fuel cells, the condensate of atmospheric moisture contains an unusually wide variety of compounds of an organic nature. The mineral portion consists practically solely of ammonia. To get rid of the ammonia, it is desirable to use highly acid cationites of the KU-2 type or to use the complex-formation method.

We know that the cations of transition metals such as copper, zinc, cobalt, silver and some others, can yield complexes with ammonia -- ammoniates (B'yerrum, 1961). The formation of ammoniates in the general form can be represented by the reactions:

$$Me^{+m} + NH_3 \rightleftarrows [Me(NH_3)]^{+m}$$
$$[Me(NH_3)]^{+m} + NH_3 \rightleftarrows [Me(NH_3)_2]^{+m}$$
$$[Me(NH_3)_{n-1}]^{+m} + NH_3 \rightleftarrows [Me(NH_3)_n]^{+m}$$

Under certain conditions, the ions of the metals listed above can bind 4, 5 or 6 molecules of ammonia.

Since ammoniates are soluble compounds, it is desirable to use the cations in the $Me^+$-form to extract ammonia in the form of complexes. In view of the high degree of stability of copper-ammonia complexes, preference must be given to the $Cu^+$-form of the cationite. Binding of the ammonia by the cation of the transition metal in this case is described by the expression:

$$R_2Cu + 4NH_3 \longrightarrow R_2Cu(NH_3)_4.$$

The effect of increasing the exchange capacity of the $Cu^+$-form of the cationite in comparison with the $H^+$-form of the cationite in extracting ammonia is shown in Figure 4 (Yegorova, Krasnoshchekov et al., 1970; Khomchenko, Chizhov, Sinyak et al., 1971). The conditions for the determination of the capacity of the cationites were as follows. The volume of resins in the $H^+$ or the $Me^+$-form was 20 ml, the ratio of the height of the layer to the diameter (1/d) was 10, the rate of penetration was 100 ml/hour. The concentration of ammonia was determined by the titrimetric method using phenolphthalein.

From Figure 4 it follows that the most effective of the cationites is KU-2X16 in the Cu-form, whose total exchange capacity for ammonia was found to be 3.35 mg·eq/ml in comparison with 1.53 mg·eq/ml for KU-2X16 in the $H^+$-form.

Cationites in the $Me^+$-form can theoretically be used for the regeneration of water from solutions whose composition includes nitrogenous compounds that have an unshared pair of electrons, but it must be taken into account that the /67
aliphatic amines, for example, coordinate with more difficulty than ammonia and form less stable complexes.

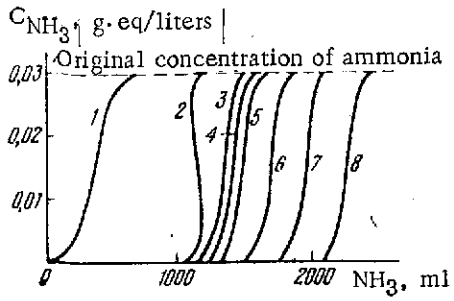


Figure 4. Output Curves for Sorption of Ammonia From an Aqueous Solution by Cationites. 1, KU-2X16 (Mg); 2, KU-2X8(H); 3, KU-2X8 (Cu); 4, KU-2X16 (Co); 5, JU-2X16 (H); 6, KU-2X16 (Ni); 7, KU-2X16 (Zn); 8, KU-2X16 (Cu); ($C_{NH_3}$ = 1,000 mg/liter; 1/d = 10; throughput = 100 ml/hour).

All of the impurities dissolved in a condensate of atmospheric moisture can be divided into the following classes:

Nitrogenous compounds (amines, ammonia, etc.);
Organic acids of the aliphatic, naphthene and aromatic series;
Hydrocarbons (saturated acyclic, saturated alicyclic, unsaturated olefinic and polyenic, aromatic);
Alcohols;
Ethers (simple, complex);
Carbonyl-containing compounds.

Organic acids are absorbed well by anionites, such as the following for example: AV-17, AN-31, EDE-10P. The exchange capacity can then reach (for example for EDE-10P relative to acetic acid) 5.5-6.0 mg·eq/gram (Saldadze et al., 1960). The absorptive capacity of ion-exchange resins relative to other classes of impurities is shown below.

| Compound | AN-31 | AV-17 | EDE-10P |
|---|---|---|---|
| Cyclopentene | 0 | 2.5 | 0 |
| Cyclopentadiene | 1.5 | 2.0 | 4.0 |
| Cyclohexadiene-1,3 | 0 | 0.9 | 2.9 |
| Cyclohexadiene-1,4 | 0 | 0 | 0 |
| Benzene | 0 | 0 | 0 |
| Di-n-butyl ether | 2.4 | 0 | 1.9 |
| n-butyl acetate | 0 | 0 | 2.7 |
| Acetone | 170.0 | 139.0 | 24.0 |
| Acetaldehyde | 202.0 | 183.0 | 169.0 |
| Alcohols, $C_1$-$C_3$ | 0 | 0 | 0 |

These values for the exchange capacities were obtained in static conditions. Studies were performed in flasks with a capacity of 200 ml each, with carefully fitted ground-glass stoppers; 150 ml of a solution with an impurity concentration of 150 mg/liter had the absorbent added to it and was subjected to continuous extraction for 48 hours.

It follows from these data that the anionites are the most effective substances for removal of acetone and acetaldehyde, while the neutral hydrocarbons are practically not absorbed at all. Since ion exchange resins are effective in the removal of electrolytes, it is difficult to use them in water /68

regeneration systems for the purpose of extracting hydrocarbons that make up part of the products of human vital activity and the waste products from biological and technical systems. In this case, it is advantageous to use activated charcoal. The use of charcoal is dictated by the need to absorb organic compounds given off by the ion-exchange resins into the solution.

The quantity of impurities to be extracted from an aqueous solution by a surface of activated charcoal is a function of the interaction energy between the water and the impurity, the charcoal and the impurity, and the charcoal and the water. Since charcoal is a hydrophobic sorbent, the latter interaction does not play an important role in sorption. However, in the case of such sorbents as silica gel and zeolites, this is very significant. Due to the considerable similarity of zeolites and silica gels to water, they cannot be used to extract organic impurities from aqueous solutions.

At the phase boundary between the surface and the solution, an adsorption potential is developed which, according to Polanyi et al., (1928) is expressed by the equation:

$$E = RT \log \frac{C_{sat}}{C_x},$$

where $C_{sat}$ is the concentration of a saturated solution of the substance to be absorbed and $C_x$ is its equivalent concentration.

It follows from the equation that the smaller $C_{sat}$ is, the lower the solubility will be and the smaller the adsorption potential; consequently, for substances with low solubility in water (for example, hydrocarbons) charcoal with a low adsorption potential should be used. In the case of substances that are readily soluble in water, it is necessary to use charcoal with a high adsorption potential.

The activity of the charcoal is primarily a function of the degree of development of a fine porous structure in it. There are three types of pores: micropores, transitional pores and macropores. The micropores, whose dimensions are commensurate with the size of molecules ($10^{-8}$ cm), are useful for adsorption of low-molecular organic substances.

In the micropores, processes of absorption of organic substances take place whose basis lies in the interaction between energetically unsaturated atoms of carbon and molecules of the sorbent. The specific nature of micropores is such that the molecule of the impurity "penetrating" the micropore is subjected to the action of powerful fields from the two opposite walls of the surface, thereby increasing adsorption.

Adsorption of organic substances by charcoal can be accomplished in two ways:

under static conditions (carbonation process);

under dynamic conditions (in carbon filters). The second version is most /69
suitable for water regeneration systems under weightless conditions. The Shilov-Voznesheskiy equation is valid for describing the operation of an adsorption carbon filter under dynamic conditions, when an important role is played by kinetic factors (Shilov, Lepin', Voznesenskiy, 1949):

$$Q = KL - \tau,$$

where Q is the time of the protective action of the layer of charcoal; L is the depth of the layer; K is the coefficient of the protective action; $\tau$ is the loss of time of protective action (the time of formation of the sorption front).

The coefficient of protective action K, expressed by the equation

$$K = \frac{\Gamma}{vC},$$

is directly proportional to the specific sorption $\Gamma$, inversely proportional to the original concentration of solution C and the filtration rate of v (in linear units per unit area of filter cross section).

The correct operation of the charcoal filter is determined by a combination of the following factors:

- the rate of diffusion of the substance from the volume to the surface,
- the rate of diffusion in the pores,
- the rate of the sorption process. Under spaceflight conditions, such requirements as the following must be added to these factors:
- increased mechanical strength of the charcoal, ensuring stable functioning of the filter under vibrational stresses;
- resistance to radiation effects;
- chemical stability of the charcoal, preventing the loss of harmful impurities into the drinking water.

In the wide range of known activated charcoals (BAU, AR, AG-3, AG-5, OU, KAD-iodic, SKT, saran, Kostochkov, A-alkaline, activated anthracite, etc.), the most important are the types of charcoal which possess a high level of mechanical strength and microporosity. However, the lack of data on the sorptive capacities of charcoal relative to individual components and the total of the impurities, as well as the lack of data on the mechanical and radiational resistance in aqueous media do not allow preference to be given to any particular kind of charcoal.

It should be pointed out that elimination of the entire range of organic impurities with one variety of charcoal is difficult. The optimum arrangement clearly would be a layer that was composed of several types of charcoal: microporous for eliminating low-molecular impurities, large-pore for extracting high-molecular compounds.

The following are the sorption capacities (in mg/liter) of activated charcoal relative to certain organic impurities which are found in the condensate of atmospheric moisture. The conditions are static.

The results of these studies indicate that the greatest sorptive capacity /70
for the majority of components is exhibited by AG-5 and BAU charcoal. In contrast to ion-exchange resins, activated charcoal is characterized by high sorptive capacity with respect to neutral hydrocarbons.

| Compound | BAU | AG-3 | SKT | AG-5 |
|---|---|---|---|---|
| Cyclopentene | 20.5 | 21.0 | 26.5 | 26.5 |
| Cyclopentadiene | 33.0 | 18.4 | 18.4 | 22.5 |
| Cyclohexadiene-1,3 | 21.5 | 13.2 | 9.4 | 19.8 |
| Cyclohexadiene-1,4 | 34.4 | 20.6 | 20.6 | 19.4 |
| Benzene | 47.2 | 44.9 | 45.5 | 44.8 |
| Di-n-butyl ether | 47.2 | 41.9 | 46.5 | 41.3 |
| n-butyl acetate | 46.5 | 25.8 | 25.0 | 23.5 |
| Isopropyl alcohol | 10.5 | 7.5 | 9.0 | 9.0 |
| n-butyl alcohol | 21.2 | 14.3 | 18.4 | 19.3 |
| Isoamyl alcohol | 15.7 | 2.2 | 13.5 | 17.9 |
| n-heptyl alcohol | 17.4 | 17.4 | 14.5 | 11.6 |
| Ethyl alcohol | 10.5 | 7.5 | 9.0 | 9.0 |
| Methyl alcohol | 1.9 | 0 | 0 | 2.1 |
| Acetone | 9.0 | 3.7 | 4.8 | 8.5 |

Activated charcoal exhibits a low absorptive capacity with respect to alcohols and in some cases even exceeds the capacity of ion-exchange resins. The low alcohols, ethanol and methanol, pose the greatest difficulty as far as elimination is concerned.

## Distillation, Vacuum Distillation and Lyophilization (Sublimation, Molecular Drying)

### Distillation at Atmospheric Pressure

Distillation at atmospheric pressure is one of the best developed methods for separating impurities in chemical technology (Kasatkin, 1938). In fact, distillation was first used for extracting water from urine (Sendroy, Collison, 1959). However, simple distillation of urine at atmospheric pressure and a temperature of 100° yielded a condensate with a sharp odor of ammonia, increased oxidability and high pH values. Preliminary treatment of the urine with sulfuric acid, a mixture of sulfuric acid and potassium bichromate, as well as potassium persulfate somewhat decreased the concentrations of the impurities in water obtained from urine, but this water did not correspond to the generally accepted sanitary and hygienic requirements imposed on drinking water.

According to the data used by the authors of the present monograph, the chemical composition of water extracted from urine using the method of

distillation at atmospheric pressure under boiling conditions is characterized by the following parameters:

| | | | |
|---|---|---|---|
| Oxidizability, $O_2$ mg/liter: | | Ammonia, mg/liter | 1,500 |
| bichromate | 650 | pH | 12 |
| permanganate | 80 | Odor, points | > 5 |

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To make such water potable, it is necessary to use a great deal of ion-exchange resin and activated charcoal. The amount of impurities in the regenerated water can be reduced if we lower the temperature of the dilution process with evaporation in a current of air, using vacuum distillation and sublimation. The use of the evaporation process in a stream of air (Putnam, 1965) at temperatures below 65° made it possible to reduce considerably the amount of impurities in the condensate.

A shortcoming of this method is the need to work with large amounts of air. This involves the use of mechanical filters for preventing the entry of urine into the condenser. In addition, the condensate which is obtained under these conditions requires additional processing by ion-exchange resins and activated charcoal. Nevertheless, a device which is based on evaporation in air can provide 98% extraction of water from urine, requiring a power of 80 watts for 540 ml of water in one hour at a weight of 44.3 kg.

Vacuum Distillation

In the case of spacecraft, where it is difficult to use high temperatures, it is advantageous to employ water supply systems that are based on evaporation under vacuum conditions -- vacuum distillation and sublimation.

Carrying out the distillation process under reduced pressure conditions has a number of advantages over other methods of water regeneration. Thus, the boiling point of solutions decreases with reduced pressure. This makes it possible to prevent the decomposition of such labile chemical compounds as urea. In addition, vacuum distillation makes it possible to use heat-exchange apparatus with a reduced heat-transfer surface, since a considerable temperature differential is produced between the heat source and the boiling solution.

Since the process of vacuum distillation takes place at low temperatures, the heat losses to the environment and consequently the amount of heat conducted will be reduced in comparison with ordinary distillation.

Vacuum distillation as used for the regeneration of water from waste aboard a spacecraft has characteristic features. The usual concept of distillation is of a process involving the separation of liquid mixtures into fractions of different compositions. The products of human vital activity and the waste products from biological and technical systems contain a small amount (by weight) of fluid components. Therefore the role of vacuum distillation in this case amounts to a separation of the water from the dissolved salts and solids. The method of vacuum distillation for purposes of water regeneration from urine has been used by Bambenek and Zeff (1959).

/72

In so-called "passive" devices, described by these authors (Figures 5 and 6), evaporation of urine took place at a temperature of 25° and a pressure of 3 mm Hg. They proposed using the surface of the non-illuminated side of the spacecraft which is at low temperature, as a condenser. Since evaporation and condensation were accomplished by using foam, the device theoretically could work under weightless conditions. The principal shortcomings of this method are the large size of the system, due to the laws of heat exchange, and the need for orientation of the entire spacecraft in order to ensure cooling of the condenser on the dark side.

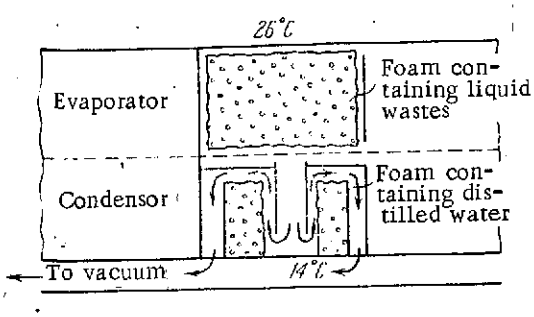


Figure 5. Diagram of a "Passive" System For Water Regeneration Under Weightless Conditions.

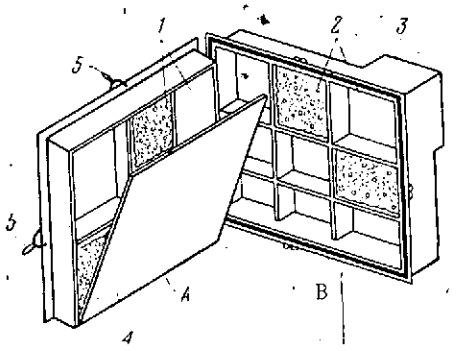


Figure 6. External View of a "Passive" Device for Water Regeneration Under Weightless Conditions. A, Evaporator; B, Condenser; 1, Foam containing liquid wastes; 2, Sterile foam for regenerated water; 3, Radiational panel; 4, Filter screen; 5, Clamps.

A device based on the method of vacuum distillation was designed and tested in a spacecraft simulator by Welch, Morgan and Ulvedal (1961). Products of human vital activity (urine, condensate of atmospheric moisture, as well as water used for sanitary and hygienic purposes) were treated with sulfuric acid to produce a pH of 2-3 and then filtered. The filtrate was placed in a still and the water extracted at 35-37°C and reduced pressure. The output of the device was 300 ml/hour and it used a power of 220 watts. The system was functional under terrestrial conditions. /73

Regenerated water in an amount equivalent to 50% of the daily norm was used by two subjects for 30 days. The authors found that water produced from wastes by the method of vacuum distillation corresponded to sanitary and hygienic requirements.

This work contains no data on the selection of optimal regeneration conditions and evidently the main purpose of the study that was performed was to determine the theoretical possibility of using purified water for human needs.

The method of vacuum distillation, combined with high-temperature pyrolysis of organic compounds, was described by Konikoff and Reynolds (1961) and by Hendel (1962). At 60 mm Hg and pyrolysis temperatures of 520-1,100° the authors obtained water from urine that was suitable for drinking. The authors point out that the device built according to this principle is characterized by considerable energy expenditure and the latter could possibly be provided for example by nuclear power sources (SNAP-8, etc.). In fact, the temperatures of 520-1,100° that were required to perform the water regeneration process complicate the use of these methods at the current level of development of power supplies aboard spacecraft. /74

The method of vacuum distillation has been studied most completely by Yu. G. Nefedov et al. Using a distillation temperature of 25-35° and a vacuum of 30 mm Hg, the authors succeeded in obtaining a condensate from urine whose principal impurity was ammonia and a small amount of organic compounds. After treating the condensate with ion-exchange resins and activated charcoal, they obtained water which completely satisfied the requirements of the All Union State Standard.

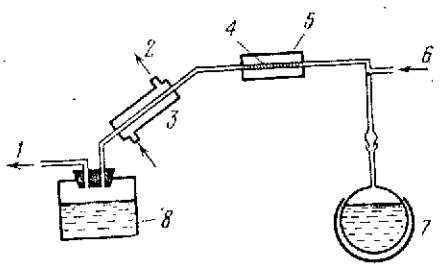


Figure 7. Device for Regeneration of Water From Urine Using The Method of Vacuum Distillation: 1, Vacuum; 2, Coolant; 3, Condenser; 4, Platinum screen; 5, Stove; 6, Air; 7, Heater; 8, Regenerated water.

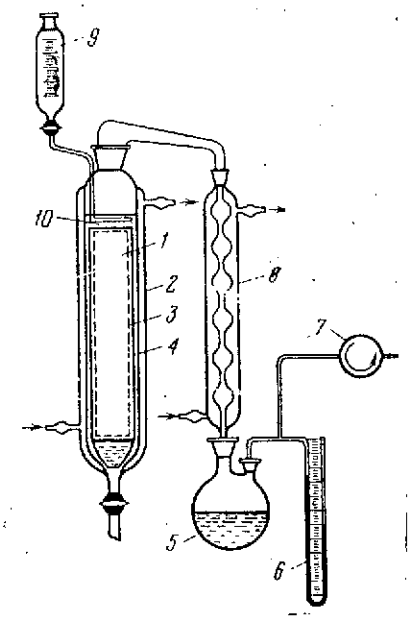


Figure 8. Diagram of a Laboratory Device for Regeneration of Water From Wastes Using the Method of Vacuum Distillation. 1-2, Evaporator; 3, Metallic screen; 4, Hydrophilic material; 5, Water collector; 6, Manometer; 7, Vacuum pump; 8, Condenser; 9, Collector for raw material; 10, Distributor for raw material.

The authors of the present monograph studied the process of water regeneration using the method of vacuum distillation by means of a device whose arrangement is shown in Figure 8 (Moisayev et al., 1967). The vacuum distillation method has a number of shortcomings as well as certain advantages. For example, it is practically impossible to get rid of dissolved volatile substances which have a boiling point close to that of water by using

vacuum distillation. In this case, it is necessary to use either a unit for additional sorption purification or extensive oxidation. The organization of the condensation process and the production of fluid under vacuum and weightless conditions poses considerable difficulty. The use of the vacuum of space to avoid depressurization of the spacecraft appears problematical. However, the engineering and design problems will be overcome in the future and the method of vacuum distillation may become one of the most suitable approaches to the regeneration of water.

Lyophilization (Sublimation, Molecular Drying)

The unit for supplementary purification in regeneration systems may be reduced considerably in size if we use sublimation (lyophilization, molecular drying). The lyophilization method consists in using a process of separation of the solid, liquid and gaseous phases by means of free evaporation in a high vacuum.

The mechanism for the separation of the components of the solutions under these conditions differs from the processes that are carried out at atmospheric pressure or a low vacuum. Distillation at atmospheric pressure, for example, is usually performed under conditions that involve boiling of a fluid, when its vapor tension is equal to the outside pressure. The vapor phase has a composition that corresponds to the ratio of elasticity of the saturated vapors of the components. The transfer of the vapor from the evaporator to the condenser is effected by diffusion. Decreasing the pressure above a boiling fluid causes the average free path length of its molecules to increase. At $10^{-3}$-$10^{-4}$ mm Hg the average molecular free path length may become equal to the length of the tubing. Under these conditions the molecules of the evaporating component will leave the evaporation surface practically without colliding. In this case the transition of the molecules takes on the form /75
of molecular flow, in which the rate of evaporation of the substances will be determined only by the rate of thermal motion of the molecules.

The process of sublimation (lyophilization) usually takes place under conditions of a vacuum of $10^{-3}$-$10^{-4}$ mm Hg at reduced evaporating temperatures. By means of this method, it has become possible in the food and medicine industries to dehydrate a number of products (juices, bread, milk, antibiotics and so forth), whose drying by thermal methods would be either undesirable or impossible (Lykov, Gryaznov, 1956). However, under these conditions the attention of the researchers was directed only to the quality of the product being dehydrated without a determination of the optimum conditions for obtaining pure water.

The method of lyophilization as it applies to water supply systems for the crews of spacecraft was first studied by Sandroy and Collison (1959). By sublimating frozen urine in a high vacuum, the authors obtained water that was characterized by an unpleasant odor and taste. Processing the urine and the condensate that was obtained with activated charcoal enabled the authors to obtain "very pure water, suitable for human needs".

Sublimation of a mixture of urine and feces results in water that has negative organoleptic characteristics.

After Kryuchkov, Chizhov and Moiseyev, who used a special design of lyophilic regeneration systems, it became possible to obtain from urine water that required practically no sorption purification. A diagram of this system can be seen in Figure 9. Products of human vital activity which contain moisture are placed in evaporators (sublimators) 1 and frozen. After freezer 4 has been filled with a coolant (in this case, a mixture of "dry ice" and ethyl alcohol), the vacuum pump is switched on. Water vapor is frozen on the surface of the freezer and the salts and organic compounds remain in the evaporator-sublimator. When all of the water has been separated, the system is filled with air; when the ice thaws, the water which is formed runs off into collector 2. /77

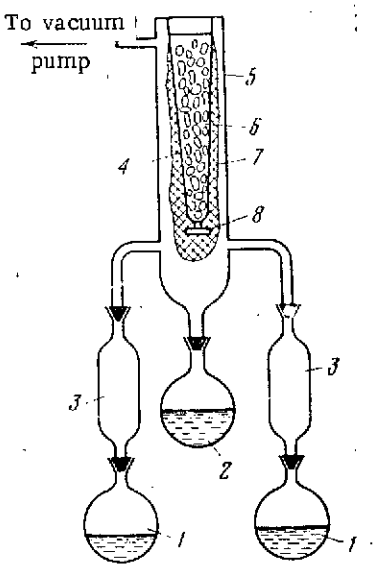


Figure 9. Diagram of a Device for Regeneration of Water by the Lyophilization Method (Sublimation, Molecular Drying): 1, Evaporators; 2, Water collector; 3, Trap; 4, Condenser-freezing trap; 5, Cylindrical housing; 6, Coolant; 7, Ice; 8, Disc for supporting ice.

The technology for the regeneration of water by using the method of lyophilization can be simplified somewhat if the stage of preliminary freezing is eliminated. When urine is evaporated in a high vacuum, the application of external heat cannot compensate for the heat that is lost through evaporation and the original solution begins to lower the temperature until ice forms.

By means of this system, the possibility of obtaining water from the following vital activity products was studied: urine, feces, a mixture of urine and feces, a condensate of atmospheric moisture, solutions of urine and feces that had been subjected to microbiological mineralization using an aerobic method, suspensions of chlorella, potato tops, potato peelings and carrot tops. The results of these studies are shown in Table 14 (Koloskova et al., 1967).

It follows from the table that the concentration of the impurities in water regenerated by the lyophilization method is low and a small amount of ion-exchange resin and activated charcoal is required to bring the quality of the water up to generally accepted standards.

TABLE 14.* QUALITY OF WATER OBTAINED BY THE LYOPHILIZATION METHOD FROM VARIOUS MOISTURE-CONTAINING PRODUCTS OF HUMAN VITAL ACTIVITY AND WASTE PRODUCTS FROM BIOLOGICAL SYSTEMS.

| Parameters | Possible sanitary standards | Water | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | From urine | From feces | From a solution of urine and feces | | From a suspension of chlorella | From potato tops | From potato peelings | From the condensate of atmospheric moisture |
| | | | | Not processed | Following aeration | | | | |
| pH | 6—8 | 6 | 6,5 | 6 | 6 | 6 | 6 | 6 | 7 |
| Oxidizability, mg $O_2$ $O_2$/l | 6 | 2,9 | 52,83 | 2,88 | 10,8 | 4,75 | 5,5 | 19,6 | 80,4 |
| Nitrogen from ammonia, mg/l | 1 | 2,8 | 30,0 | 13,5 | 2,48 | 2,5 | 7 | 1,4 | 35 |
| Nitrogen from nitrates, mg/l | 0,1 | 0,004 | 0,03 | 0,1 | 0,35 | 0,01 | 0,12 | 0,02 | 0,015 |
| Nitrogen from nitrates, mg/l | 40 | 0,1 | 0,12 | 10,2 | 0,5 | 0,12 | 0,23 | 0 | 0 |
| Total nitrogen, mg/l | — | 3 | — | 28 | — | — | 14 | 2 | — |
| Organic nitrogen, mg/l | 0 | 0 | — | — | — | — | — | — | — |
| Chlorides, mg/l | 200 | 7,1 | — | 3,5 | 8,9 | 0 | — | 10,6 | — |
| Sulfates, mg/l | 80 | 0 | — | 10,5 | 13,4 | 0 | Traces | Traces | 0 |
| Phosphates, mg/l | 0,1 | 0,02 | 0,035 | 0,05 | — | 0,017 | 0 | 0,025 | 0,01 |
| Total hardness, mg·eq/l | 7 | 0 | — | 0 | 0 | 0 | Traces | Traces | 0 |
| Calcium, mg·eq/l | 4 | 0 | 0 | 0 | 0 | 0 | Ditto | Ditto | 0 |
| Magnesium, mg·eq/l | 2 | 0 | — | 0 | 0 | 0 | » | » | 0 |
| Potassium, mg/l | — | 0 | — | 0 | 0 | 0 | 0 | — | 0 |
| Sodium, mg/l | Ditto | 0 | — | 0 | 0 | 0 | 0 | — | 0 |
| Transparency, cm | 25 | 25 | 25 | 25 | 25 | 25 | 25 | Cloudy | 25 |
| Chromaticity on the platinum-cobalt scale, degrees | 10—15 | 12 | 10 | 15 | 10 | 15 | 10 | Ditto | 10 |
| Odor at 20°, points | Up to 2 | 0 | Pungent | 5 | 5 | 3 | 4 | 3 | 2 |
| Cloudiness, mg/l | — | 0 | 0 | 0 | 0 | 0 | 0 | Cloudy | 0 |
| Precipitate, mg/l | — | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Suspended substances, mg/l | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Urea, mg/l | 0 | 4,9 | 0 | — | — | — | — | — | — |
| Uric acid, mg/l | 0 | 0 | — | — | — | — | — | — | — |
| Creatinine, mg/l | 0 | 0 | — | — | — | — | — | — | — |
| Alcohols, mg/l | — | — | — | — | — | — | — | — | 550 |
| Microbial contamination, microbes/ml | 100 | $10^2$ | — | $10^3$ | $10^3$ | — | — | — | — |

*Note: Commas indicate decimal points.



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Experimental data were obtained with a condensation-freezing temperature of -78°, an evaporation-sublimation temperature of -3 to (-15°), and a vacuum of $10^{-2}$ mm Hg. It follows from Table 14 that on the basis of the principal parameters, the water obtained from products of human vital activity and biological systems corresponds to generally accepted requirements. Some variations can be seen in the case of regeneration of water from feces. However, the use of ion-exchange resins and activated charcoal has made it possible to obtain water that is completely in accord with the requirements of the All-Union State Standards.

Regardless of the definite advantages of the method of lyophilization in terms of the quality of the regenerated water in comparison with other methods, it is a very difficult matter to use it as the basis for the system for a water supply during spaceflight. This is due to the need to eliminate heat from the condenser at low temperature, which requires the use of large radiating areas (up to 0.74 $m^2$ per man according to Hendel, 1964). In addition, the use of low temperatures for freezing out water vapor assumes an orientation of the spacecraft which is not always possible. When using the vacuum of space, the necessary loss of uncondensed molecules must be taken into account (for example nitrogen, oxygen, carbon dioxide, and several other compounds), as well as water in proportion to the vapor tension at the temperatures employed. Some of these shortcomings can be overcome by using small vacuum pumps and refrigerators. /78

The Vapor-Compression Method

The vapor-compression method of water regeneration involves the following stages: 1) vacuum distillation; 2) compression of vapor and 3) condensation of vapor using the latent heat of condensation to heat the waste products subjected to regeneration. Compressed vapor has a high temperature in comparison with the original solution and serves for heating the original liquid, thereby acting as a heat pump.

An example of the use of the vapor-compression method for purposes of regenerating water from urine is a device whose layout is diagrammed in Figure 10 (Hendel, 1964). Waste products are placed in evaporator 1, where compressor 2 is used to produce rarefaction. At 27 mm Hg and cabin temperature, the water from the waste products begins to boil. By means of compressor 2, the vapor is compressed; the temperature of the latter is raised to 32°. The hot vapor then passes through a coil in evaporator 1 where heat is given off to the original solution and the vapor is condensed. The condensed fluid enters the filter for removal of organic and inorganic impurities. Under weightless conditions, it is necessary to use a rotary evaporator and condensor in this device in order to separate the fluid from the noncondensed gases.

R. A. Bambenek and I. D. Zeff (1961) have described a device which works on the vapor-compression principle, intended for operation under weightless conditions. The device has the following parameters: weight 20 kg, power 150 watts, output 4.5 kg per cycle, cycle length 6 hours, degree of extraction of water from urine 84%, cabin air loss less than 0.04 kg per cycle. To /79

decontaminate the urine and reduce the odor, a quaternary ammonium base is used -- "hyamine 1622". Reduction of foaming and splashing of urine into the compressor and condenser is achieved by using "granulated anti-foaming agent C".

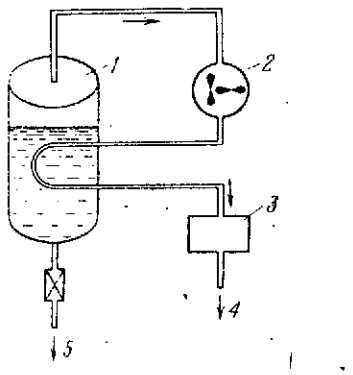



Figure 10. Diagram of a Device for Regeneration of Water by the Vapor-Compression Method.
1, Evaporator; 2, Compressor or fan; 3, Filter; 4, Distillate; 5, Concentrate.

Despite its obvious advantages, the vapor-compression method also suffers from such shortcomings as the need to use a rotary evaporator and condenser, and the likelihood of waste particles entering the compresser and putting it out of commission. In addition, the regeneration system itself, based on the vapor-compression method, will not yield water that is capable of satisfying sanitary and hygienic requirements. In order to bring the resultant condensate up to acceptable drinking conditions, it is necessary to have an additional purification unit.

The Oxidation-Catalytic Method

The oxidation-catalytic method consists in conversion of all volatile toxic, ill-smelling and biologically active compounds of organic and inorganic origin into simple oxides or elements. Since these compounds are composed of nitrogen, hydrogen, carbon, oxygen and sulfur, their oxidation will result in the formation of water, carbon dioxide, nitrous oxides, sulfur and molecular nitrogen. Carbon dioxide is eliminated by absorbers that are widely used in life support systems. The amount of sulfur compounds is volatile and gaseous substances contained in urine, the condensate of atmospheric moisture, water used for hygienic and sanitary purposes and other wastes is small, so that the development of considerable concentrations of sulfur oxides in the regenerated water is low. The oxides of sulfur and nitrogen, entering the water as sulfites, sulfates, nitrates and nitrites, can easily be moved by ion-exchange resins.

The oxidation-catalytic method may be accomplished either at atmospheric or superatmospheric pressures. Regeneration systems that are designed on the basis of this method are simple and include the following: evaporator, catalytic reactor, condenser, clean water receptacle, blower. Oxidation of all volatile substances takes place in a stream of air on the surface of a heterogeneous catalyst.

Literature on the total oxidation of organic compounds which are contained in the products of human vital activity and the wastes from biological and technical systems is sparse. We know that methane, for example, is oxidized on copper (more than 200°), molybdenum (300°), silver (320°), vanadium and platinum catalysts (480°) (Alekseyevskiy et al., 1937). It has been found that

acetic acid yields carbon dioxide and water on magnesium-chromium and carbon--chromium catalysts; methyl-ethyl ketone, butyric aldehyde and ether are burnt to form mixtures of organic acids (Margolis, Todes, 1949).

In choosing catalysts for the regeneration of water from waste, one can use data obtained as the result of extensive studies of the catalytic oxidation of carbon monoxide in processing cartridges for gas masks (Alekseyevskiy et al., 1937; Kats, 1955) as well as in the catalytic oxidation of exhaust fumes from internal combustion engines (Sokol'skiy, Popova, 1970). A great many catalysts have been produced for oxidizing CO: Pt, Pd, oxides of manganese, copper, nickel, chromium, silver, cobalt and so on. However, maximum activity is seen in those catalysts which are based on the oxides of manganese, copper, cobalt and silver -- the hopcalites (Fraser et al., 1919; Bray, 1920). These catalysts oxidize carbon monoxide even at negative temperatures, a fact that is quite rare in catalytic chemistry. /80

The principal component of hopcalites is active magnesium oxide. The oxides of copper, cobalt and silver act as promoters. Two types of hopcalites exist:

- hopcalite 1, which consists of 50% $MnO_2$, 32% CuO, 15% $Co_2O_3$ and 5% $Ag_2$;
- hopcalite 2, consisting of 60% $MnO_2$ and 40% CuO.

It has subsequently been found that 4-component hopcalite has no important advantages over 2-component hopcalite. The principal shortcoming of hopcalites is their being made poisonous by water vapor. However, as further studies have revealed, this effect is only observed in a catalytic process that occurs at low temperature (below 100°). At temperatures above 100° the poisonous qualities are considerably reduced, indicating the possibility of using hopcalite in systems for regenerating waste.

The high temperatures of the catalytic process (400-500°) may cause a breakdown of the active manganese dioxide. However, the precise dissociation temperature of $MnO_2$ has not been established. The initial dissociation temperatures of $MnO_2$, according to the data of various authors (Alekseyevskiy et al., 1937), are shown below.

| Author | Temperature, °C |
|---|---|
| Meyer, Rogers | 530 (in air) |
| Askinazi, Klonovskiy | 565 (in oxygen) |
| Zakur, Bar | 572 (at 816 mm Hg) |
| Kendall, Fuchs | 420 (at 760 mm Hg) |
| Muassan | 290 |
| Wright, Luft | 390 |
| Gorgen | 400 |
| Gempel' | 470 |
| Drucker, Huttner | 15 (at 501.5 mm Hg) |
| Zimon, Fekher | 518 |
| Blyumental' | 386 |

Probably the differences in dissociation temperatures may be explained by the different conditions under which the $MnO_2$ was prepared. In view of the fact that manganese dioxide is more stable in the presence of promoters, it can be assumed that hopcalite will work in the temperature range from 140° without decomposing. It is interesting to note that when $MnO_2$ is heated to 480° the dissociation process is reversible (Drucker, Huttner, 1929). This fact is of great importance for the regeneration of the catalyst being processed. However, even when hopcalite is processed in a temperature range of 700-850°, it is still not observed to be completely deactivated if subsequent catalytic observation is carried out at 250-300°. /81

The literature contains considerable material on the oxidation of exhaust gases from internal combustion engines (Sokol'skiy, Popova, 1970) as well as individual organic compounds (Margolis, 1967; Alanova, Margolis, 1968; Boreskov et al., 1968; Anderson et al., 1961; Royter et al., 1945). The properties of catalysts of oxidizers have been described in detail in the monograph by O. V. Krylov (1967) and the handbook edited by Royter (1968). From the data presented in these sources it follows that oxide catalysts are suitable for the oxidation of organic compounds (oxides of manganese, vanadium, chromium, nickel, cobalt, silver and so forth) metallic catalysts (on the basis of platinum and palladium), as well as complex compounds of the spinel type -- copper-chromium, iron-chromium, manganese-silver, iron-aluminum, copper--aluminum and other catalysts.

For regeneration of water from human vital activity products, there are obviously many catalysts which can be used. However, the oxides have the greatest advantage. Catalytic oxidation on oxide catalysts occurs at lower temperatures. In theory, it is possible to perform the process in an oxygen-free medium by using the oxygen in the catalysts.

At the present time, an oxide catalyst, hopcalite, most fully satisfies the requirements of water supply systems aboard spacecraft. Figure 11 shows a diagram of a regeneration system of the closed type which uses the oxidation process in the presence of oxide catalysts (Sinyak, Chizhov, 1964; Bobe et al., 1965; Moiseyev et al., 1967). The method by which water is regenerated in this device is the following.

Moisture-containing products of vital activity 4 are placed in evaporator 1 from receiver 2 and heated to the necessary temperature. When blower 8 is switched on, the air passing through the evaporator is enriched with water vapor and volatile compounds and enters a previously heated catalytic reactor 18. In reactor 18, on the surface of a heterogeneous catalyst 19, the organic substances are oxidized to form $CO_2$, $H_2O$ and the oxides of sulfur and nitrogen. As it passes through the catalytic reactor 18, the water vapor is condensed in a refrigerator-condenser 14 to form water which runs into collector 9.

The method employed for the operation of a closed-type device (Figure 12) is similar to the above. The only difference is that air continuously pumped in from the atmosphere is used to oxidize the organic compounds. Following /82

the stage of drying and purification of the air, it returns from the regeneration system to the atmosphere of the spacecraft cabin. The external appearance of laboratory devices based on the oxidation-catalytic method is shown in Figures 13 and 14.

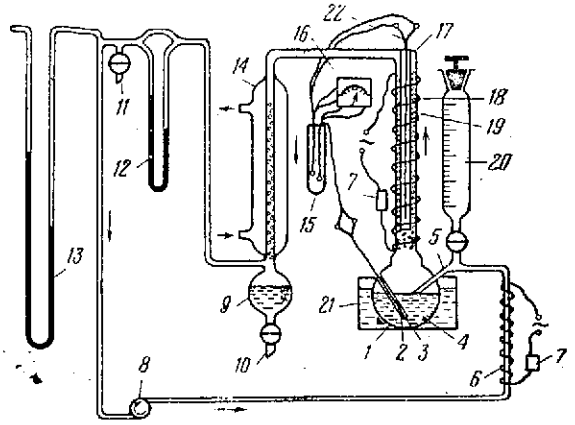


Figure 11. Diagram of a System (Closed Type) for the Regeneration of Water by the Oxidation-Catalytic Method.
1, Evaporator; 2, Thermocouple; 3, Thermocouple pocket; 4, Products of vital activity; 5, Air inlet; 6, Heater; 7, Thermostats; 8, Blower; 9, Receiver; 10,11, Stopcocks; 12, Rheometer; 13, Manostat; 14, Condenser; 15, 16, Temperature adjustment of reactor and evaporator; 17, Thermocouple pocket; 18, Reactor; 19, Catalyst; 20, Waste receiver; 21, Evaporator heater; 22, Thermocouples.

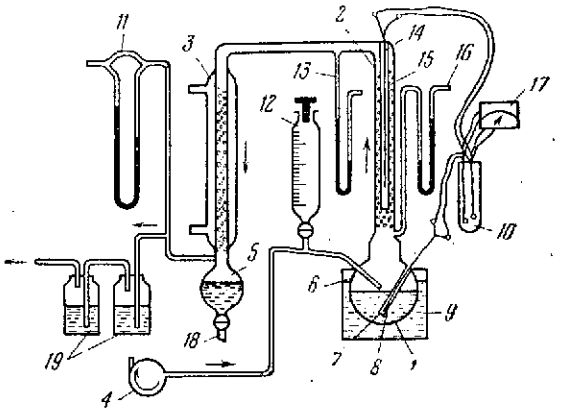


Figure 12. Diagram of a Device (Closed Type) for the Regeneration of Water by the Oxidation-Catalytic Method.
1, Evaporator; 2, Catalytic reactor; 3, Condenser; 4, Blower; 5, Receiver; 6, Air inlet; 7, 14 Thermocouple pockets; 8, Thermocouples; 9, Evaporator heater; 10, Dewar vessel; 11, Rheometer; 12, Urine receptacle; 13, 16, Manometer; 15, Catalysts, 17, Thermostat; 18, Ground-glass stopcock; 19, Bubblers.

In developing the oxidation-catalytic method of regeneration of water, /83
special attention must be paid to the selection of catalysts. Table 15 shows the results of a chemical analysis of water obtained from urine in the presence of various catalysts. The data in Table 15 were obtained under the following conditions: weight of catalyst, 100 grams; consumption of vapor-gas-air medium, 4.0 liters per minute; evaporation temperature 100°, condensation temperature 15 to 20°, temperature in the zone of the catalyst, 150°.

It follows from the table that in the presence of hopcalite or the oxides /84
of copper, chromium or nickel, water which resembles distilled water in terms of its composition is obtained from urine. The only exception is ammonia, whose amounts vary from 30 to 40 mg/liter.

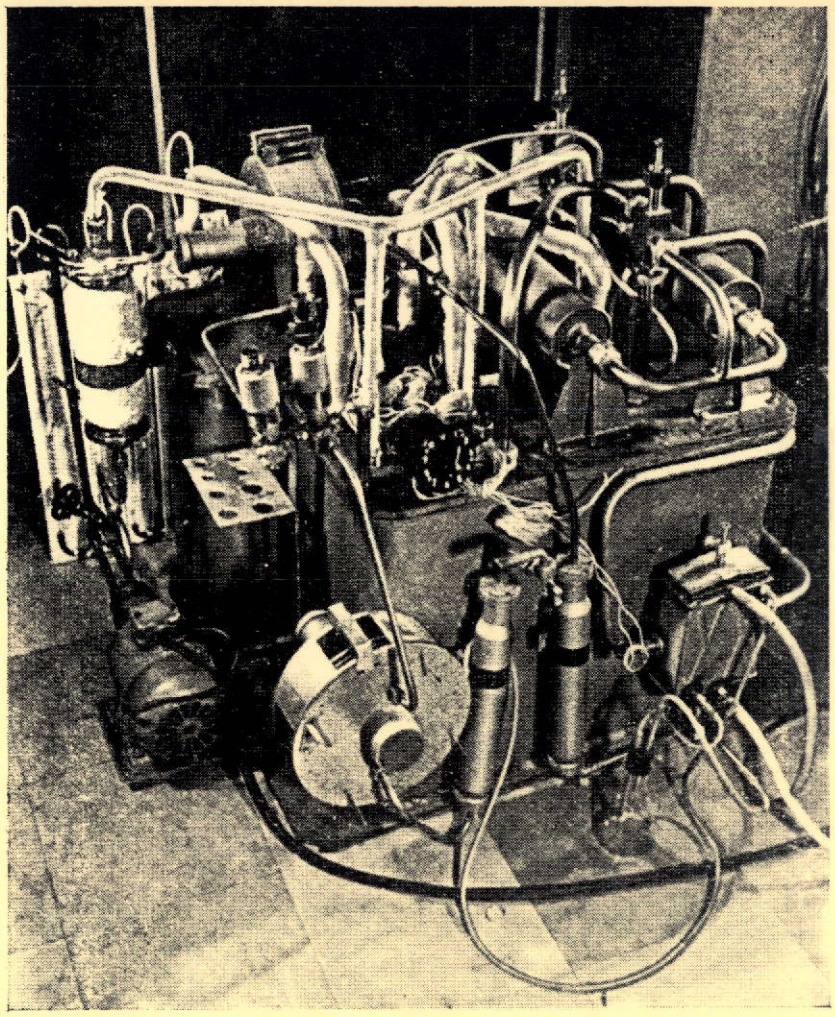


Figure 13. External View of a Laboratory Device for Regeneration of Water by the Oxidation-Catalytic Method.

In the presence of platinum and palladium, the condensate obtained from urine has a sharp odor of urine indicating incomplete oxidation of the organic foul-smelling compounds at the temperatures employed. However, Konikoff and Reynolds (1961) have shown that at 520-1,100° platinum screens make it possible to obtain from urine water which satisfies criteria rendering it fit to drink. /85

Since a real water regeneration system must be characterized by minimal energy consumption, it is extremely important to know the initial temperatures in the zone of the catalyst at which the process of oxidation of the volatile substances in the urine takes place. Table 16 presents the results of studies conducted by the authors of the present paper dealing with the influence of catalyst temperature (hopcalite) on the chemical composition of the water obtained from urine (conditions same as before).

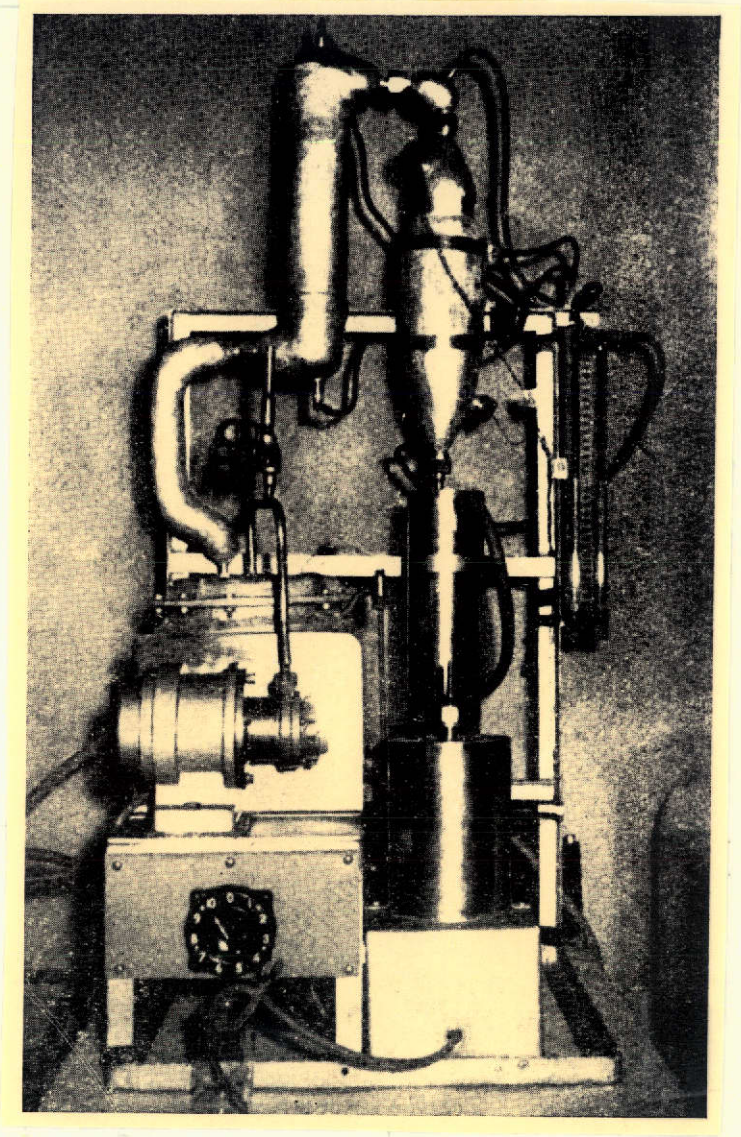


Figure 14. External View of an Experimental Device Based on the Oxidation-Catalytic Method.

It follows from Table 16 that at temperatures up to 100° in the catalyst zone the condensate which is obtained has a sharp odor of urine, increased oxidability (26 mg $O_2$/liter) and ammonia (up to 80 mg/liter). However, at 100° the volatile compounds of urine begin to be oxidized to a large extent on the surface of the catalyst, the odor of urine disappears, the amount of ammonia decreases and reaches 35 mg/liter at 150°, which can easily be eliminated by means of cationite.

TABLE 15.* CHEMICAL COMPOSITION OF WATER OBTAINED FROM URINE ON VARIOUS CATALYSTS

| Catalyst | Parameters of water quality | | | | | | |
|---|---|---|---|---|---|---|---|
| | pH | Oxidizability (permanganate), mg $O_2$/l | $NH_3$, mg/liters | $NO_2$, mg/liters | $NO_3$, mg/liters | Odor, points | Hardness, mg·eq/liters |
| Hopcalite | 7,1 | 1 | 32 | 0,07 | 0,4 | 0 | Traces |
| Coper oxide and chromium oxide (Spinel) | 7,1 | 1—2 | 30 | 0,02 | 0,6 | 0 | Ditto |
| Oxides of nickel and chromium (Spinel) | 7,1 | 1—2 | 40 | 0,09 | 0,4 | 0 | » » |
| Platinum on ceramic | 7,5 | 24 | 72 | 0,1 | 0,2 | 5 | » » |
| Palladium on ceramic | 7,5 | 25 | 81 | 0,2 | 0,3 | 5 | » » |

Note: Commas indicate decimal points.

TABLE 16. INFLUENCE OF CATALYST TEMPERATURE ON CHEMICAL COMPOSITION OF WATER PRODUCED FROM URINE

| Temperature of catalyst, °C | Parameters of water quality | | | | | |
|---|---|---|---|---|---|---|
| | pH | Oxidizability (permanganate), mg $O_2$/l | $NH_3$, mg/liters | $NO_2^-$, mg/liters | $NO_3^-$, mg/liters | Odor, points |
| 70 | 8,0 | 26 | 75,0 | 0,08 | 0,2 | Odor of urine |
| 80 | 7,6 | 25 | 80,0 | 0,5 | 0,2 | Odor of urine |
| 100 | 7,6 | 10 | 57,0 | 0,06 | 0,3 | 2 |
| 120 | 7,6 | 9 | 50,0 | 0,1 | 0,3 | 0 |
| 130 | 7,6 | 8 | 40,0 | 0,06 | 0,4 | 0 |
| 140 | 7,5 | 5 | 35,0 | 0,07 | 0,4 | 0 |
| 150 | 7,3 | 2 | 35,0 | 0,08 | 0,6 | 0 |
| 200 | 7,2 | 2 | 20,0 | 1,5 | 36,0 | 0 |
| 400 | 4,5 | 14 | 3,0 | 11,0 | 41,0 | 0 |
| 500 | 3,0 | 18 | 0,0 | 13,0 | 62,0 | 0 |

*Note: Commas indicate decimal points.

The pattern of the change in the oxidability of the water is interesting. The increased levels of oxidability in the temperature range from 70-100° are due to incomplete oxidation of volatile compounds. In the range from 120-200°, we find the minimum oxidability values. It would be natural to expect that increasing oxidation temperature to 400-500° would result in a more extensive oxidation process and, as a result, zero oxidability values. However, at temperatures of 400-500°, there is a clearly pronounced increase in the oxidability of the water (up to 14-18 mg $O_2$/liter). This may be explained by the fact that at high catalyst temperatures there is a predominance of the reaction involving oxidation of ammonia to form the oxide and dioxide of nitrogen: /86

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$
$$2NO + O_2 \longrightarrow 2NO_2.$$

Nitrous oxide, which oxidizes to form nitrogen dioxide, forms anions of nitric acid $NO_2^-$ in an aqueous solution:

$$2NO_2 + H_2O = H^+ + NO_2^- + H^+ + NO_3^-.$$

In determining oxidability in terms of the permanganate method, some of the $KMnO_4$ goes to oxidize the nitrite anion, producing a simulation of the presence of organic compounds in the water. In reality, the water obtained from urine at 400-500° contains practically no organic substances and the nitrite ions can easily be eliminated by anionite.

On the basis of the temperature relationship set forth in Table 16, we can conclude that the optimum temperature for oxidation must be 150°. In this case, the oxidability of the water does not exceed the requirements of the All-Union State Standard for drinking water, and the amount of ammonia is small. Although increasing the temperature of the catalytic oxidation causes total elimination of ammonia and total oxidation of organic compounds, preference must be given to performing the regeneration process at 150° because considerable increases in energy consumption are observed at high temperatures.

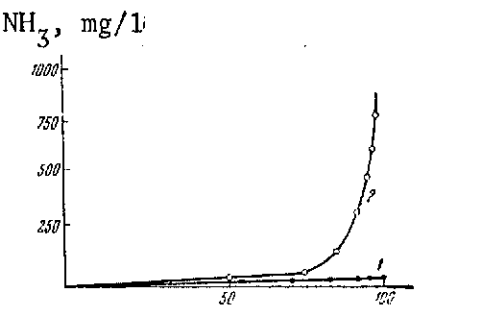



Figure 15. Change in Ammonia Concentration in Regenerated Water as a Function of the Degree of Extraction of Water From Urine.
1, Concentration of ammonia in water obtained under the conditions of a working reactor; 2, Same, obtained with the catalytic reactor shut off.

The quantity of $NH_3$ in the regenerated water is a function not only of the oxidation temperature but also of the amount in the urine. The principal source of the $NH_3$ that gets into the circulating branch of the water regeneration system is urea. The effect of the hydrolysis of urea with formation of $NH_3$ and $CO_2$ is particularly evident under the prolonged influence of high temperatures and an increase in the concentration of the solid residue of urine. Figure 15 shows the dependence of the ammonia concentration in the regenerated water on the degree of extraction of water from urine (Belyakova, Sinyak, 1967). It follows from the illustration that up to 80% extraction of water from urine does not contribute a significant amount of ammonia to the condensate. After 80% extraction has been reached, there is a sharp jump in $NH_3$ concentration in the regenerated water. It should be pointed out that this occurrence is not observed if the water regeneration process using urine is

/87

carried out under reduced evaporation temperature or pressure conditions (Table 17). Results shown in the table indicate that under the conditions of reduced evaporation temperature and pressure of the vapor-gas-phase it is possible to obtain water that does not require additional purification and santisfies the generally accepted requirements of sanitary and hygienic standards. /88

TABLE 17.* DEPENDENCE OF CHEMICAL COMPOSITION OF REGENERATED WATER ON PRESSURE OF VAPOR-GAS PHASE AND EVAPORATION TEMPERATURE OF URINE

| Parameters | Temperature, °C | | | Pressure, mm Hg | |
|---|---|---|---|---|---|
| | 50 | 100 | Flame of gas burner | 500 | 350 |
| pH | 6,5 | 7,1 | 10 | 6,5 | 6,5 |
| Oxidizability, permanganate, $O_2$, mg/liters | 1,5 | 2,0 | 44 | 1,0 | 1,0 |
| Nitrogen from ammonia, mg/liters | 1,2 | 40,0 | 1500 | 1,0 | 1,0 |
| Nitrogen from nitrites, mg/liters | 0,02 | 0,03 | 0,5 | 0,01 | 0,01 |
| Nitrogen from nitrates, mg/liters | 0,4 | 0,4 | 41 | 0,3 | 0,3 |
| Chlorides, mg/liters | — | 50 | 124 | 20 | 30 |
| Urea, mg/liters | 0 | 0 | 0 | 0 | 0 |
| Transparency, cm | 30 | 30 | 30 | 30 | 30 |
| Chromaticity, degrees | 15 | 15 | 15 | 15 | 15 |
| Odor, points | 0 | 0 | Pronounced odor of ammonia | 0 | 0 |
| Microbial contamination, microbes per ml | 0 | 0 | 0 | 0 | 0 |

*Note: Commas indicate decimal points.

The oxidation-catalytic method may be used for regeneration of water from other moisture-containing products of human vital activity and waste products from biological systems. Table 18 shows the results of the use of the oxidation-catalytic method to obtain water from a condensate of atmospheric moisture, water used for sanitary and hygienic purposes, fugate from a chlorella suspension, and solutions of urine and feces mineralized by the microbiological method (Moiseyev et al., 1967). The conditions for regeneration are the same as above.

Hence, the oxidation-catalytic method possesses a certain degree of universality and may be considered a promising method for use when there is a sufficient supply of thermal energy aboard.

Methods of Semipermeable Membranes

The essence of the method of semipermeable membranes consists in the separation of aqueous solutions by means of membranes which are selective with respect to a certain class of chemical compounds.

TABLE 18.* CHEMICAL COMPOSITION OF WATER OBTAINED FROM VARIOUS MOISTURE-CONTAINING WASTES BY THE OXIDATION-CATALYTIC METHOD

| Parameters | Condensate of atmospheric moisture | | Water used for sanitary purposes | | Fugate of chlorella suspension | | Mineralized solution | |
|---|---|---|---|---|---|---|---|---|
| | 1* | 2 | 1 | 2 | 1 | 2 | 1 | 2 |
| pH | 6 | 6,5 | 8 | 6,5 | 7,0 | 6,0 | 8 | 6,0 |
| Oxidizability, $O_2$ mg/liters | 248 | 2,0 | 289 | 1—3 | 56,5 | 1—6 | 242 | 0,8 |
| Nitrogen from nitrites, mg/liters | 10,0 | 0 | 0,5 | 0,1 | 9,6 | 1 | 0,2 | 0,1 |
| Nitrogen from nitrates, mg/liters | 10,0 | 0,8 | 100 | 10,1 | 195 | 4,0 | 80 | 0,1 |
| Chlorides, mg/liters | — | 0 | 170 | 10,0 | 5,68 | 4,0 | 337 | 15 |
| Urea, mg/liters | — | 0 | — | 0 | — | 0 | — | 0 |
| Transparency, cm | — | 30 | — | 30 | — | 30 | — | 30 |
| Chromaticity, degrees | — | 10 | — | 10 | — | 10 | — | 10 |
| Hardness, mg·eq/liters | — | 0 | — | 0 | — | 0 | — | 0 |
| Odor, points | 5 | 0 | 5 | 0 | 4 | 0 | strong | 0 |

* 1, Prior to regeneration; 2, after regeneration.

*Note: Commas indicate decimal points.

There are two types of membrane methods which are most promising:

- evaporation through a membrane,
- reverse osmosis (ultrafiltration, hyperfiltration).

Method of Evaporation Through a Membrane

The method of evaporation through a membrane is based on the selective passage of components through a polymer membrane with subsequent evaporation at reduced barometric pressure or by directing a flow of an inert gas over the surface of a film. The energy expenditure involved in separation by this method is determined primarily by the energy required for evaporating the mixture passing through the film.

The method of evaporation through a membrane is used quite widely in the chemical industry for separating azeotropic mixtures, aqueous solutions of alcohols, etc. (Kahlenberg, 1906; Binning et al., 1961; Dytnerskiy et al., 1961). Such polymer films as cellophane, polyethylene, teflon, saran, "ftorlon" and many others are used as semipermeable membranes.

The mechanism of separating solutions by the method of evaporation through membranes has not yet been completely explained. Thus, Binning et al., (1961) feel that the separation may be explained by the presence in the swelling film of a "solution phase" and a "vapor phase zone". Diffusion in the "vapor phase zone" determines the rate of the entire process. The selectivity is produced by a phase boundary within the membrane. Long (1968) explains the reason for the selectivity as a difference in the coefficients of diffusion

of individual components. In the opinion of Madras (1949), the flow of the liquid in the swollen cellophane is capillary. Ticknor (1958) feels that the nature of the flow of water in membranes is capillary while the flow of alcohols is by diffusion. Schrot et al., (1961) suggests that the selectivity of separation is governed by the possibility of formation of a hydrogen bond between the components to be separated and the material composing the film. According to the data of Volgin et al., who used the device shown in Figure 16, the mechanism of the passage through cellophane and cellulose acetate membranes is capillary, with a minor role being played by the diffusion current.

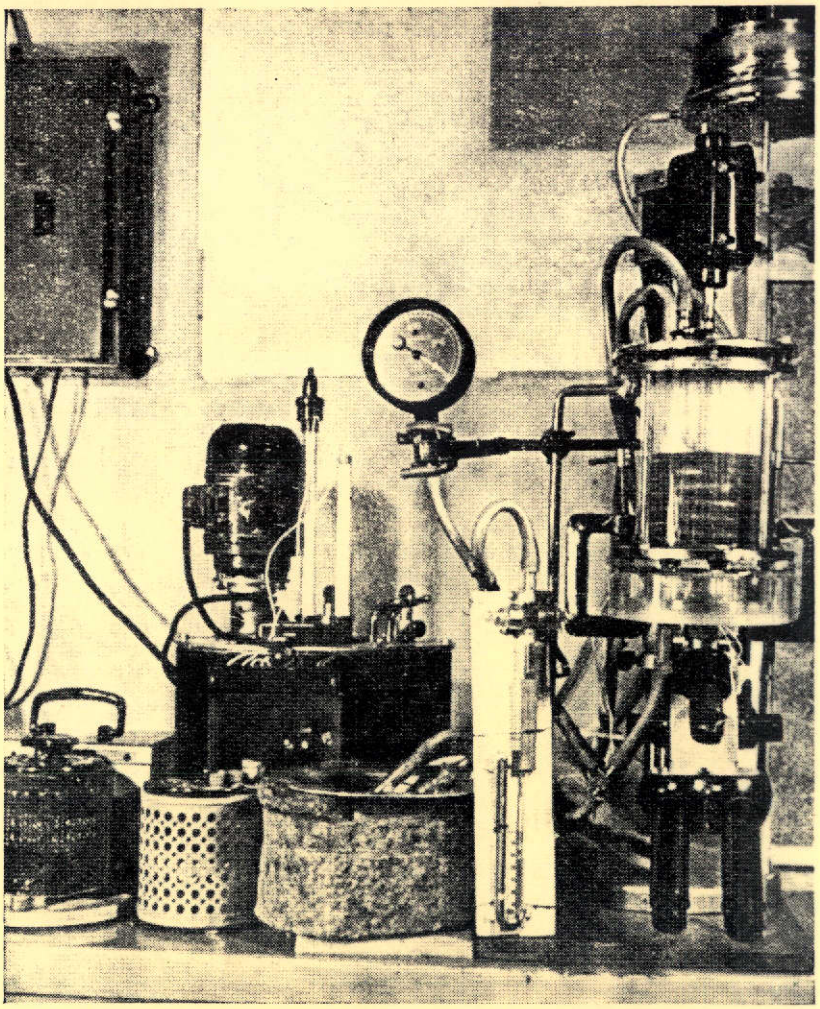


Figure 16. External View of a Laboratory Device for Regeneration of Water by the Method of Evaporation Through a Membrane.

Hence, there is no unanimity of opinion at the present time with respect to the mechanism of separation, which complicates the selection of effective membranes for separation of solutions in general and for regeneration of water from wastes in particular. However, there is a rule confirmed by a number of investigators that can be used: the component which is more soluble in the polymer will pass through more rapidly; this makes it possible to limit the number of polymer materials which can be used in water supply systems. Obviously, hydrophilic films are most convenient, such as cellophane, cellulose acetate, films made of polyvinyl alcohol, polyacrylonitrile and several others.

Koenikoff and Miller (1965) used the method of evaporation through a membrane for water supply systems for the purpose of regenerating water from urine. The laboratory device is simple in design. Its principal elements are /90
a steel container with a membrane fastened across the neck, a condenser and a receiver. The waste products of vital activity, for example human urine, are placed in the container and the system is then pumped out with a vacuum pump. The pressure in the system is held at 40-50 mm Hg, at which point the boiling point of urine is 40°. The total surface area of the membrane is 85 $cm^2$. /91
Under these conditions, the output is 190 mm of water per hour.

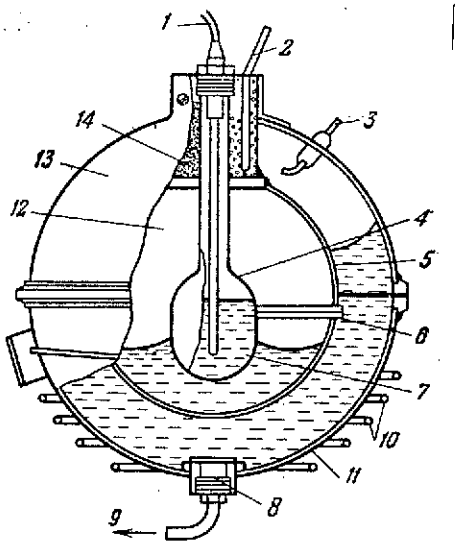



Figure 17. Diagram of Experimental Apparatus for Regeneration of Water From Urine Using the Method of Evaporation Through a Membrane. 1, Source of electrical energy; 2, Filler; 3, To vacuum; 4, Electrical heating element; 5, Double walls; 6, Clamps; 7, Heating wall; 8, Drain for condensate; 9, To regenerated water containers; 10, Coolant; 11, External covering; 12, Urine evaporating chamber; 13, Condenser; 14, Semipermeable membrane.

The authors constructed a device for regenerating water by the semipermeable membrane method which was capable of operation under weightless conditions (Figure 17). The device is spherical in shape and can produce up to 9 liters of water per day. The heating element, located in the spherical housing, is mounted inside the evaporating chamber. The size of the surface area of the spherical covering is chosen with an eye toward effective heating of the urine. Between the spheroidal covering and the heating element is a heat conductor -- a fluid that possesses considerable thermal conductivity. The device is made of stainless steel. The evaporating chamber is made of two hemispheres with double walls; this is necessary in order to remove the dense residue of the urine. The semipermeable membrane is mounted in the neck at the top of the evaporating chamber. The condensation chamber is made in the shape of

a hemisphere which facilitates removing it from the system. The power requirement for 24 hours is 300 watts.

The considerable advantage of this method of evaporation through a membrane is the possibility of carrying out the operation under weightless conditions, since the membrane automatically acts as a separator between the liquid and vapor-gas phases. Regardless of the comparatively mild conditions of the water regeneration process, this method does have shortcomings which slightly complicate its use in water supply systems designed for spacecraft crews: it has a low level of water extraction, a possibility of plugging of the membrane pores by organic compounds and salts, and the limited mechanical strength of the membranes. /92

Method of Reverse Osmosis

The method of reverse osmosis has been given practically no attention in conjunction with processes of desalination and purification of water under terrestrial conditions. Thus far, no mechanism for the process of separation of solutions by the method of reverse osmosis has been developed. In order to clarify this mechanism, several hypotheses have been proposed. One of the first was the hypothesis of ultrafiltration (screening), which holds that only molecules smaller than the diameter of the pores can pass through the membrane (Spigler, 1960). However, examples of separation of mixtures are known in which the molecules held back by the membrane are much smaller than the pores (Kommermeyer et al., 1955). The diffusion hypothesis does not always hold up either (Madras et al., 1949); it holds that selectivity is explained by the difference in the coefficients of diffusion of the individual components. The selectivity of the membranes can be explained to a certain extent by the hypothesis of Raid (Raid, Spencer, 1960) which holds that there are two types of water in the structure of the membranes: bound and free. The binding of the water is caused by hydrogen bonds. The bound water loses its hydrational ability and consequently cannot act as a solvent. When it is in the pores, the bound water acts as a selective barrier: when external pressure is applied, only pure water will pass through such a membrane, continuously forming and breaking down hydrogen bonds as it goes.

Sourirajan (1963) suggests a sorption mechanism for selectivity on the basis of the Gibbs equation:

$$U = -\frac{1}{RT}\left[\frac{\partial\sigma}{\partial \ln a}\right]_T \cdot A,$$

where U is the adsorption of salts, $\sigma$ is the surface tension of the solution, R is the gas constant and T is the absolute temperature, A is the surface area of the solution and a is the activity of the salts. It is suggested that the boundary layer of the solution, which is in contact with air or with an appropriate membrane, is impoverished with respect to the dissolved substance (thanks to negative adsorption). The layer of solution which is near the membrane will consist of pure water. In the event that the diameter of the

pores in the membrane is not greater than twice the thickness of his layer, by applying pressure to the solution practically pure water can be obtained from the other side.

To confirm the correctness of any hypothesis, it is necessary to establish the nature of the flow of the liquid through polymer membranes. Of the two possible mechanisms of flow [diffusion and capillary (viscous)] the latter is clearly more probable. A proof of this is the relationships that have been found between permeability and selectivity and pressure, temperature, position of the membrane in the cell, etc. (Dytnerskiy et al., 1968; Lukavyy, Sinyak, Chizhov, 1970; Dytnerskiy, Kukavyy, Sinyak, 1970). /93

Figure 18 shows a diagram of a device for the regeneration of water using the reverse osmosis method, which made it possible to study these relationships. The operating principle of the device is the following. The moisture-containing products of human vital activity are placed in a container 3 and transported by a piston pump through filter 2 into separating cell 6. The purified water, passing through the membrane of the cell, enters a receptacle 8 while the concentrate moves on to the input of storage container 3. To reduce concentration polarization, a magnetic stirrer 10 is used. A hydraulic accumulator 4 is used to reduce energy consumption. The change in membrane permeability with respect to NaCl as a function of temperature (Figure 19) is inversely proportional to the viscosity of the solution (in the range from 10 to 50°). When 85° is reached the membrane becomes impermeable. This effect is explained by the contraction of the pores in the membrane in the course of the structuring of the polymer.

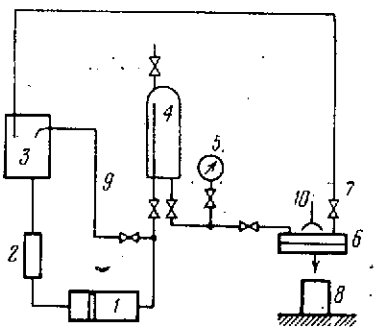



Figure 18. Diagram of a Device for Regenerating the Water by the Method of Reverse Osmosis.
1, Piston pump; 2, Filter; 3, Supply container; 4, Hydraulic accumulator; 5, Manometer; 6, Separating cell; 7, Throttle valve; 8, Collector; 9, Bypass line; 10, Magnetic stirrer.

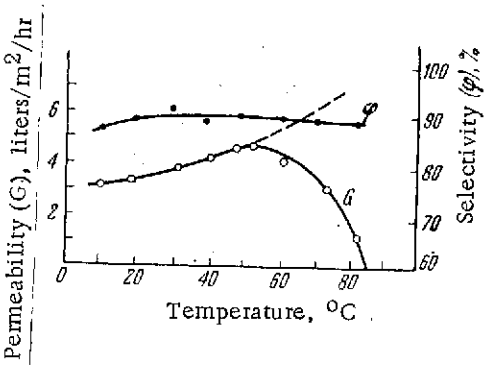



Figure 19. Selectivity and Permeability of a Cellulose Acetate Membrane Versus Temperature.
$\phi$ - Selectivity
G - Permeability

Figure 20 shows the relationship of permeability and selectivity of membranes with respect to N and Cl versus external pressure. In the 100-200 atm range there is a peak on the permeability curve which can be explained by the compaction of the capillary-pore structure of the polymer at high pressures. With a capillary type of flow of the solution, the selectivity of the membrane may be explained by data on the bound fluid (Dumanskiy, 1960; Deryagin, Churayev, 1967). /94

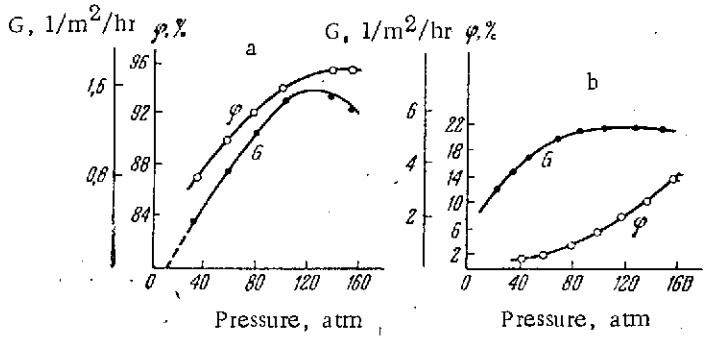



Figure 20. Permeability and Selectivity Versus Pressure (Experiments Without Mixing; System -- 1% Aqueous NaCl Solution. a, Cellulose acetate membrane No. 5 ($\phi$ = 95%, p = 100 atm); b, Membrane made of regenerated cellulose. Symbols same as in Figure 19.

The surface of the membrane and of the capillaries is covered with a layer of bound fluid which has a reduced dissolving capacity. Therefore, the membrane will be selective if it has pores that are not greater than twice the thickness of the layer of bound fluid.

It follows from Figure 20 that as the external pressure rises the selectivity changes from 0 to some constant value. This can be explained by the rise in the bound water fraction in the membrane due to deformation of its pore structure. An increase in the concentration of the solution leads to a decrease in selectivity; this is explained by a decrease in the thickness of the layer of bound fluid. The use of the method of reverse osmosis for regeneration of water from products of human vital activity has proved its feasibility. Thus, Lukavyy (1969) showed that by using this device at a constant static pressure of 100 atm at room temperature it is possible to obtain water that contains no more than 5% impurities relative to the original contamination level. The chemical composition of water obtained from urine by the method of reverse osmosis is shown in Table 19.

The method of reverse osmosis as it applies to water supply systems for spacecraft crews has a number of advantages, of which the most important are the following:

- low energy consumption;
- performance of the process at low temperatures, preventing breakdown of many labile compounds;
- possibility of using the muscular effort of cosmonauts.

However, a number of shortcomings inherent to reverse osmosis decrease the value of this method somewhat. For example, we still do not know of any membranes that can hold back such compounds as urea. The degree of extraction of the water is comparatively low and can reach 80% in the case of urine. Moreover, the membranes that are used (cellophane, cellulose acetate and others) are insufficiently strong. Mechanical strength can be increased by using capillary membranes made of porous glass (Guter, Bittman, 1967). /95

TABLE 19. SOME PARAMETERS OF THE CHEMICAL COMPOSITION OF WATER OBTAINED FROM URINE BY THE METHOD OF REVERSE OSMOSIS

| Days | Oxidizability, permanganate, $O_2$ mg/liter | Nitrogen from ammonia, mg/liter | Chlorides, mg/liter | Permeability, $l/m^2$/hour |
|---|---|---|---|---|
| 1 | 99 | 20 | 603 | 0.37 |
| 8 | 81 | 11 | 348 | 0.24 |
| 16 | 45 | 18 | 249 | 0.25 |
| 24 | 123 | 22 | 416 | 0.26 |
| 32 | 89 | 21 | 426 | 0.24 |
| Average for 32 days | 95 | 21 | 419 | 0.25 |

Despite these shortcomings, the method of reverse osmosis could evidently be used for the regeneration of such moisture-containing products of vital activity as the water used for sanitary and hygienic purposes, impoverished nutrient solutions from lower and higher plants and other wastes characterized by large mass for which methods of evaporation would be unfeasible.

Electrochemical Methods of Water Regeneration

Electrodialysis is the principal and most widely used electrochemical method of purification of aqueous solutions (Nel'son, 1963; Laskorin, 1958; Martynova, 1963). The essence of the electrodialysis process consists in the following.

If a container divided into three chambers by ion-exchange membranes is filled with electrolyte and a difference in potential is created on electrodes that are mounted in the extreme electrode chambers, the ions of the solution will begin to travel from the central chamber into the concentrating chambers. Ionite membranes mounted in the electrolytic bath have their own electrostatic charge and act as distinctive cationic and anionic filters. The cationic membranes, negatively charged, allow cations to pass through them which move toward the cathode and practically block the anions, which have the same charge, due to the forces of electrostatic repulsion. /96

The principal characteristic of the process is the fact that the level of output with respect to current is determined by the selectivity of the membrane, the level of electrostatic transport of water and the reverse diffusion of ions.

The selectivity of the membranes deteriorates as the salt content of the solution increases. This fact, together with the electrostatic transport of water through the membrane, basically determines the possible degree of concentration of the solutions. Thus, for example, 25% solutions are practically impossible to concentrate by the electrodialysis method. Relatively small energy expenditures, as well as the high current output (up to 85%) required for desalination of solutions resembling urine in their composition, indicate a certain degree of feasibility for the electrodialysis method of eliminating dissolved salts. However, the electrodialysis method is practically ineffective as far as getting rid of chemical compounds of a non-ionogenic nature is concerned (such as urea, for example). The latter, it is true, may be hydrolyzed to ammonium carbonate by means of the enzyme urease (Hawkins, 1958; Belyakova, Sinyak, 1967) or as the result of thermal hydrolysis (Belyakova, Sinyak, 1967). However, when urea is decomposed by urease there is an increase in the amounts of substances consumed, and the need to get rid of the enzyme, an organic protein substance, also arises.

Thermal decomposition is free of these shortcomings but the output of thermal energy lowers the effectiveness of electrodialysis as one of the low energy consuming methods. The most promising solution to the problem of getting rid of organic compounds of a non-ionogenic nature is their electrochemical oxidation. Inasmuch as electrochemical oxidation is similar in many respects to the action of strong oxidizers, a suggestion has been made (Glasstone, Hickling, 1939) that the hydroxyl ions in an aqueous solution are discharged with a low potential on the anode, forming hydrogen peroxide. The latter reacts with the organic depolarizer, causing oxidation or breaking down into oxygen and water. However there is evidently no unanimity of opinion as far as explaining the mechanism of all the reactions of electrochemical oxidation of organic compounds is concerned. In each individual case it is necessary to conduct a special study of the mechanism, taking many factors into account (electrode potential, composition of the electrolyte, material of the electrodes, temperature, etc.)(Milton, J. Allen, 1961).

In water supply systems for spacecraft crews the electrochemical oxidation may be of interest in connection with eliminating nonabsorbent organic impurities such as for example urea, ethyl and methyl alcohol, acetone, etc.

The mechanism of methanol oxidation was studied in a work by Khazova et al. (1965) in which it was shown that the stage which is retarded to the greatest extent is the chemical interaction between the adsorbed particles of C-OH which are formed as the result of dehydration of methanol molecules with particles of $OH_{ads}$. In contrast to the oxidation of methanol, the anode oxidation of aliphatic ketones and particularly acetone have been studied extremely little as yet. We know that oxidation in an acid medium with low current densities on the platinum electrode yields acetic and formic acid; at /97

high current densities, in addition to the above, the products of the reaction are methane, unsaturated hydrocarbons, carbon dioxide and a number of other compounds (Khomyakov et al., 1958).

It should be pointed out that the use of electrooxidation for purposes of regenerating water from human vital activity products involves the solution of an important and complicated problem -- the joint oxidation of methanol, acetone and other chemical compounds. The importance of this problem is due to the fact that in order to solve it successfully the design of the apparatus required to perform the process will be advantageously characterized by simplicity. The problem, however, lies in the fact that the optimum modes of the process of oxidation of each of these substances may differ (optimum oxidation conditions, for example for acetone in small concentrations, are not known) and in this case the search for optimum conditions will consume considerable experimental time.

Figure 21 shows the change in concentration of urea in urine as a function of the result of electrochemical oxidation. We can see from this graph that in the anode chamber of an electrolytic cell the urea concentration can be decreased from 20 to 5 g/liter in 3-4 hours. The results shown in Figure 21 were obtained with a device whose schematic diagram and external appearance are shown in Figures 22 and 23.

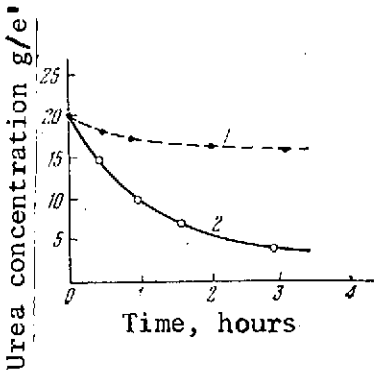



Figure 21. Change in Urea Concentration in the Urine in the Cathode and Anode Chambers. 1, Cathode chamber; 2, Anode chamber.

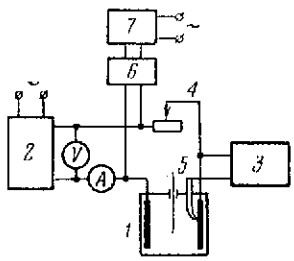



Figure 22. Diagram of Electrolytic Cell for Oxidation of Organic Compounds. 1, Electrolytic cell; 2, Rectifier; 3, Cathode voltmeter; 4, Rheostat; 5, Reference electrodes; 6, Switch; 7, Time delay relay.

One of the interesting variations of the electrochemical method of water purification that have been developed in recent years is the porous electrode method. The essence of the porous electrode method consists in using an anode and a cathode which have very complicated surfaces (Blair, Murphy, 1960; Smith et al., 1962). The solution to be purified passes over the surface of such electrodes, where transfer and induced adsorption of the ions occurs under the influence of an electric current (usually at a potential of 2-2.3 volts). Using electrodes with high porosity causes a sharp decrease in polarization. /98

As soon as the sorption capacity of the electrodes has been exhausted, it is possible to achieve desorption of the ions and thereby regenerate the electrodes by reversing the polarity.

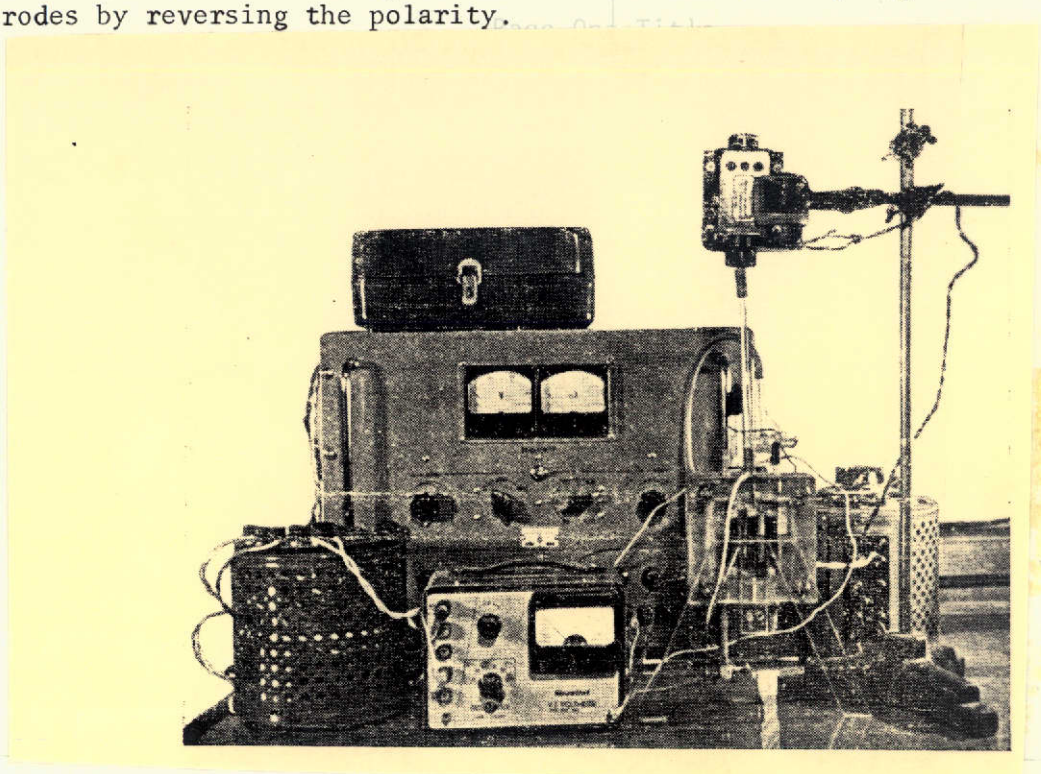


Figure 23. External Appearance of a Laboratory Device for Regenerating Water by the Method of Electrochemical Oxidation.

Porous electrodes are usually made of finely crushed carbon or colloidal graphite; the core may be made of fiberglass, dacron fiber, etc. The cation- and anion-exchange properties of porous electrodes are the result of the sulfuration of the graphite by a mixture of nitric and sulfuric acid in a proportion of 1:3 or oleum (cationitic properties), or by treating the graphite with polyethylene amine, dimethylphenylene diamine, etc. (anionitic properties).

Smith et al. (1962) described the parameters of a planned purification /99
device with an output of 380 $m^3$ of water per day. The basic element of the device was an electrochemical cell composed of a number of alternating porous electrodes, cathode and anode plates, separated by frames and separators in the housing. There could be up to 100 electrode pairs measuring 200 × 560 mm in the cell. The thickness of the anode was 0.24 mm and that of the cathodes was 0.19 mm; the distance between electrodes was 0.63 mm. The operating principle of such a device was the following.

From container 1 (Figure 24) the contaminated water is transported by means of pump 2 to filter 3, where the suspended particles are removed. After

passing through filter 3, the water reaches an electrochemical cell 4 where a process of desalination occurs on the porous electrodes, after which the purified water goes to collector 6. In order to ensure normal operation of the electrochemical cell, the polarity of the electrodes is switched every 15 minutes and the brine removed. The characteristics of the device are the following: electrode potential 0.5-1.5 volts; obtaining 1 $m^3$ of water involves expenditure of 0.7-0.8 kW/hour. The salt concentration decreases from 1.75 to 0.17 g/liter.

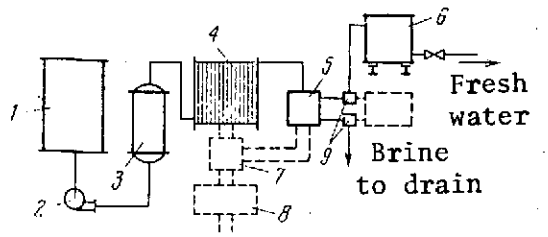



Figure 24. Diagram of Electrochemical Purification of Water.
1, Container for wastes; 2, Pump; 3, Filter; 4, Electrochemical cell; 5, Sorbents; 6, Water collector; 7,8, Supply containers; 9, Conductometer.

A modification of the porous electrode method is the method of filtering water through porous graphite electrodes to which a d.c. voltage of 1-2 volts has been applied (Yefimov, 1967).

The method of porous electrodes is suitable for purposes of regenerating water aboard manned spacecraft primarily because of its low energy consumption.

However, only ionized compounds can be extracted by means of the porous electrode method. Moreover, the degree of extraction of water in this case is low. On the whole, electrochemical methods for water supply systems designed for use by spacecraft crews have not been developed in practical form.

Regeneration of Water by the Coagulation Method

In the purification of industrial and residential waste water, the method of coagulation is used widely (Kul'skiy, 1963; Kul'skiy, Koganovskiy et al., 1950). Coagulants and auxiliary substances known as flocculants are usually /100
employed for the coagulation of water. The coagulants convert the colloidal pollutants to unstable forms and create conditions in which the process of agglutination to form a colloid structure can begin; this structure is formed through flaking. In many instances the coagulants convert the substances to be removed to compounds that are difficult to dissolve and in some cases the reagents themselves form compounds on whose surfaces the pollutants in the water are adsorbed.

The auxiliary substances are divided into adsorbents and flocculants. The former extracts the impurities from the water which are soluble in it; the latter accelerate the formation of large flakes from particles of pollutants and the products of hydrolysis of coagulants. The coagulants that are generally used in water purification include aluminum sulfate, iron chloride,

aluminum alum and a number of other substances. The cations of these salts possess the ability to lower the stability of colloid particles. However, the bases and basic salts that have low levels of solubility and are formed when these salts hydrolyze separate out from the solution in the form of large flakes, taking the colloidal impurities with them. The degree of hydrolysis is a function of a number of factors of which the pH of the medium is the most important.

The hydrolysis of aluminum sulfate takes place most completely in the pH range from 4.95 to 5.4. The optimum rate of hydrolysis of iron salts is in the pH range from 9.0 to 10.5; for sodium aluminate it is 6.4 to 7.0. If hydrolysis takes place outside these limits, large quantities of cations of aluminum or iron will remain in the solution and will exceed the permissible sanitary levels.

One of the most widely used flocculants is colloidal silicic acid -- activated sodium silicate (Kul'skiy, Nakorchevskaya, Slipchenko, 1969). The flocculent properties of this substance are most clearly evidenced at pH = 5.5.

Recently, the high-molecular organic flocculants have aroused interest. Depending on the nature of the ionogenic groups, they can be divided into anionic and cationic. With different charges on the particles of the pollutants and the polyions of the flocculants there is simultaneous flocculation and coagulation without mineral coagulants. In order to remove the positively charged inorganic impurities from water, well-known anionic flocculants are used, such as partially hydrolyzed polyacrylamide or carboxymethylcellulose.

However, runoff water which contains a large amount of organic pollutants cannot be purified completely by flocculants. Therefore, it is advantageous to use high-molecular flocculants of the cationic type which have a positive charge on the macromolecule. It has been demonstrated that using such flocculants as VA-2 and VA-3, developed at the Pamfilov Academy of Municipal Services (Veytser, 1960) result in a decrease in the weight of the coagulant by 2-6 times in comparison with aluminum sulfate.

However, the optimum effect of the action of these flocculants is obtained within very narrow pH limits. In water supply systems designed for spacecraft crews the method of coagulation may be used for regeneration of water from /101
sanitary and hygienic water supplies. The latter have colloidal compounds in their composition which can be coagulated by one of the above coagulants. The needs of spaceflight are met most completely by $Al_2(SO_4)_3$. In order to use iron chloride it is necessary to have liming or some other process to reduce the pH to levels that correspond to the sanitary and hygienic water. It is also difficult to use active silicic acid since it has the property of aging and loses its activity in 3-6 weeks. Due to the presence of a large amount of organic impurities in sanitary and hygienic water in comparison with inorganic impurities, the use of high-molecular flocculants such as polyacrylamide and carboxymethylcellulose is difficult, since they have the same negative charge as the majority of the organic impurities in the sanitary and hygienic water.

These preliminary conclusions are valid only for sanitary and hygienic water whose composition contains washing compounds with an aliphatic base. However, if synthetic surfactants (SF) are used as the washing compounds, the effectiveness of the coagulation method will be decreased sharply. The problem of eliminating SF from waste water is due to their considerable stability with respect to salts, acid solutions, alkalis, microorganisms, and their ability to form a stable foam. No reliable and effective method of getting rid of SF has been developed, even for terrestrial conditions.

However, when using natural soap with a fat base, it is possible to use coagulation as one of the low-energy consumption methods that work under weightless conditions.

Coagulation as a method of water regeneration for use under spaceflight conditions has been studied in a number of papers (Arkhangel'skaya et al., 1957; Balashova et al., 1969). It has been shown that the optimum coagulant for clarification of used sanitary and hygienic water is $Al_2(SO_4)_3 \cdot 18\ H_2O$. We can see from Figure 25 that the effective concentration of aluminum sulfate is 0.4-0.5 g/liter of purified water.

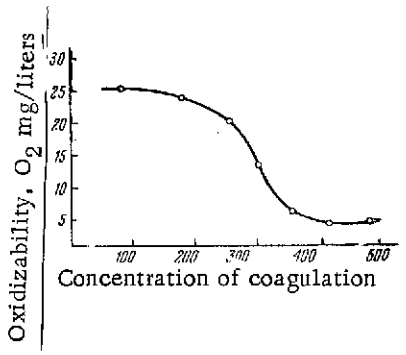



Figure 25. Change in Concentration of Organic Substances (Oxidability) in Coagulated and Filtered Water as a Function of Coagulant Concentration ($Al_2(SO_4)_3$).

It must be emphasized that using the method of coagulation will not make it possible completely to rid the solutions of inorganic and organic substances. In order to bring the quality of the water up to the required levels it is necessary to use additional purification, for example, with ion-exchange resins, activated charcoal or some other oxidative method. /102

Radioisotope Methods

The oxidation of compounds that are difficult to absorb by means of the photochemical method may turn out to be a highly effective method of purifying water. However, it is necessary to have energy expenditure in this case, although it is insignificant in magnitude. It is possible to reduce the electrical energy consumption to a minimum level if radioactive radiation is used instead of ultraviolet.

The effect of radioactive radiation on aqueous solutions is generally familiar in the nuclear industry (Allen, 1963; Kasperovich et al., 1971). The possibility of radiation oxidation of alcohols and other compounds which are difficult to absorb is of the greatest significance for water supply systems.

The principal effect of radiation on aqueous solutions of alcohols consists in the splitting off of one of the hydrogen atoms from the α-carbon

atom or from the hydroxyl group. As a result of these two processes of splitting a number of organic compounds are formed: glycols, aldehydes, ketones, acids and other substances. Thus, for example as the result of the radiation oxidation of ethyl alcohol the solution is found to contain the following after it has been irradiated: acetaldehyde, acetic acid and hydrogen peroxide (Allen, 1963). Irradiation of alcohol solutions in the presence of oxygen causes an increase in the amount of acetaldehyde. The oxygen may be replaced by other oxidizers, hydrogen peroxide for example. The latter has a number of advantages in comparison with other oxidizing substances.

Table 20 lists the results of using $\gamma$ radiation and hydrogen peroxide to oxidize compounds that are difficult to remove from a condensate of atmospheric moisture and other moisture-containing wastes. Irradiation was given in doses of 0.2 mrad; the dose level was varied from 20 to 500 r/sec; the radiation source was $Co^{60}$. The irradiated solutions were separated from the products of radiolysis by filtering through an absorbent layer composed of KU-2 cationite, AV-17 anionite and AG-5 activated charcoal (Bychkov et al., 1972).

TABLE 20.* INFLUENCE OF RADIATION DOSE AND HYDROGEN PEROXIDE CONCENTRATION ON THE PURIFICATION OF ETHYL ALCOHOL SOLUTIONS (CONCENTRATION: 1,000 mg/liter)

| $H_2O_2$ in the original solution, % | Dose, mrad | Chemical composition of irradiated solution | | |
|---|---|---|---|---|
| | | Content of $H_2O_2$, % | Oxidizability, mg·eq/liter·$10^2$ | Oxidizability of filtrate (permanganate), $O_2$ mg/liter |
| 0,1 | 1 | 0,04 | 0,63 | 418 |
| 0,2 | 1 | 0,14 | 0,59 | 429 |
| 0,5 | 1 | 0,39 | 0,67 | 463 |
| 0,1 | 2 | 0,001 | 1,32 | 141 |
| 0,2 | 2 | 0,066 | 1,48 | 29 |
| 0,5 | 2 | 0,32 | 1,34 | 19 |
| 0,1 | 3 | 0,001 | 1,46 | 218 |
| 0,2 | 3 | 0,04 | 1,62 | 11 |
| 0,5 | 3 | 0,23 | 1,65 | 2,7 |
| 0,1 | 4 | 0,001 | 1,3 | 154 |
| 0,2 | 4 | 0,025 | 1,43 | 13 |
| 0,5 | 4 | 0,208 | 1,54 | 5 |
| 0,1 | 5 | 0,001 | 1,28 | 83 |
| 0,2 | 5 | 0,015 | 1,32 | 2,6 |
| 0,5 | 5 | 0,17 | 1,43 | 0 |

*Note: Commas indicate decimal points.

As we can see from Table 20, in the case of a solution containing 1,000 mg/liter of ethyl alcohol, a dose of 2-5 mrad is required with a hydrogen peroxide concentration of 0.2%. Aqueous solutions of alcohol, containing reduced concentrations, may be purified with a lower dose. Thus, for example, for radiation oxidation of alcohol solutions with a concentration of the latter of 100 mg/liter a dose of 0.5 mrad will suffice for a hydrogen peroxide concentration of 0.02% (Table 21). It has been observed that the dose level has no

influence on the effectiveness of radiation purification: solutions irradiated with doses at the 500 and the 20 r/sec levels, with all other conditions being equal (dose, hydrogen peroxide and alcohol concentration) had a final oxidability of no more than 10 mg/liter. /104

TABLE 21.* INFLUENCE OF RADIATION DOSE AND HYDROGEN PEROXIDE CONCENTRATION ON PURIFICATION OF ETHYL ALCOHOL SOLUTIONS (CONCENTRATION: 100 mg/liter)

| $H_2O_2$ in original solution, % | Dose, mrad | Chemical composition of irradiated solution | | |
|---|---|---|---|---|
| | | $H_2O_2$,% | Oxidizability, [mg·eq/liter·$10^2$] | Oxidizability of filtrate (permanganate), $O_2$ mg/liter |
| 0,1 | 0,2 | 0,08 | 1,1 | 24 |
| 0,2 | 0,2 | 0,16 | 1,1 | 15 |
| 0,5 | 0,2 | 0,38 | 1,6 | 21 |
| 0,1 | 0,3 | 0,08 | 1,7 | 11 |
| 0,2 | 0,3 | 0,15 | 1,9 | 8 |
| 0,5 | 0,3 | 0,35 | 2,1 | 15 |
| 0,01 | 0,4 | 0,001 | 2,0 | 16 |
| 0,02 | 0,4 | 0,005 | 2,2 | 13 |
| 0,05 | 0,4 | 0,03 | 2,2 | 12 |
| 0,01 | 0,5 | 0,001 | 2,0 | 19 |
| 0,02 | 0,5 | 0,003 | 2,1 | 7 |
| 0,05 | 0,5 | 0,03 | 2,2 | 7 |
| 0,1 | 0,5 | 0,07 | 2,0 | 8 |
| 0,2 | 0,5 | 0,13 | 2,1 | 8 |
| 0,5 | 0,5 | 0,31 | 2,2 | 8 |

*Note: Commas indicate decimal points.

When ethyl alcohol is irradiated, it is oxidized practically completely to form acetic acid. In the gaseous phase, hydrogen, carbon dioxide and oxygen can be found as well. One of the sources of oxygen is hydrogen peroxide, which remains in a concentration of approximately 0.01 M/liter following irradiation; it decomposes catalytically to form water and oxygen upon filtration through a layer of AV-17 anionite.

It is advantageous to use β-radiators as sources of radioactive radiation because they require less radiation shielding than do γ-radiators. The requirements of the water regeneration system are most completely met by a strontium-yttrium source. It has a halflife of 29 years with an average radiation energy of 0.9 MeV (maximum path of the β-particles in water is 5 mm).

Despite the obvious advantages, the method of radiation oxidation has several limitations. Thus, the weight of the shielding against ionizing radiation makes it impossible to use this method on flights in the near future. However, when isotope sources of electrical energy are used, these limitations will be automatically eliminated and radiation will be one of the most feasible methods.

Radioactive isotopes can be used in water regeneration systems not only as sources of ionizing radiation but also as sources of thermal energy (Margaret, 1967; Metzger et al., 1970; Jackson, 1971).

Thus, Margaret (1967) describes a system for a device used to regenerate water from urine using plutonium-238 (Figure 26). The heat given off by the $Pu^{238}$ is used both for heating the moisture-containing products of vital activity (in this case, urine) and for pyrolysis of the organic volatile compounds in the vapor-gas phase. The distillation temperature is 66°, the condensation temperature is 33° and the pyrolysis temperature is 660°. A rhodium catalyst is used for pyrolysis. The distillation process takes place at 90 mm Hg, while condensation occurs at 10 mm Hg. The pressure drop causes the vapor to be transported from the evaporator to the condenser.

Metzger et al. (1970) have described the results of two 32-day tests and one 42-day test involving drinking-water regeneration systems. As the source of thermal energy they used $Pu^{238}$; the evaporation temperature was 25-42°, the pyrolysis temperature was 150-175°, the vacuum was 30-32 mm Hg and the catalyst was Ardox.

Figure 27 shows a schematic diagram of this device. Since a membrane was used in the evaporator to separate the liquid and vapor-gas phases, the device could function under weightless conditions. In order to increase the reliability the evaporator was duplicated. As in the previous regeneration system, the use of the vacuum of space is proposed.

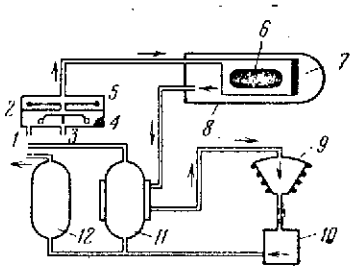



Figure 26. Diagram of a Water Regeneration System Using Heat From a Radioisotope Source.
1, Moisture-containing wastes; 2, Vapor; 3, Motor; 4,6, Radioisotope heat sources; 5, Turbine; 7, Catalyst; 8, Pyrolysis cell; 9, Condenser; 10, Pump; 11, Hot water container; 12, Cold water container.

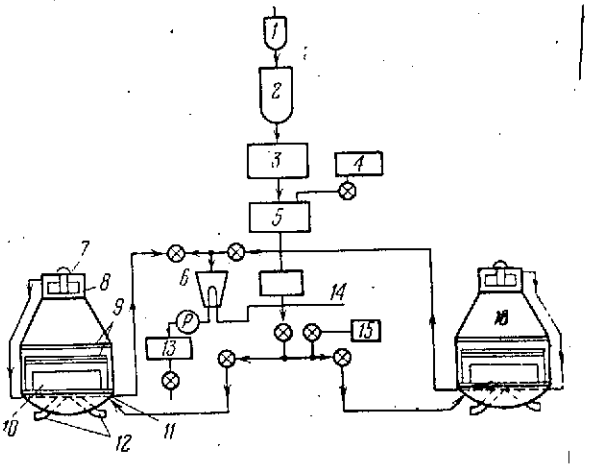



Figure 27. Diagram of a System for Regeneration of Water Using $Pu^{238}$.
1, Condensate collector; 2, Urine collector; 3, Phase separator; 4, Preliminary processing unit; 5, Container for storing urine; 6, Condenser; 7,12, Isotopes; 8, Catalytic oxidation cell; 9, Membrane; 10, Evaporator; 11, Urine; 12,13, Collector for regenerated water; 14, Pipe to vacuum of space; 15, Manometer; 16, Back-up evaporator.

The use of heat from an isotope source was described by Jackson (1971) in /105
a paper delivered at the Annual Meeting of the American Medical Association in Houston, 26-29 April, 1971. The authors discussed the results of a 90-day experiment involving four subjects. The experiment was performed with the collaboration of representatives of the United States Army, Air Force and Navy, Atomic Energy Commission, Department of Transportation, Academy of Sciences, and 30 manufacturing firms as well as seven universities. One of the tested systems was a system for regenerating water from urine. The heat from an isotope source ($Pu^{238}O_2$ with a power of 350 watts) was used to evaporate water from urine.

Hence, while the use of ionizing radiation for water supply systems is problematical, the use of radioactive isotopes as thermal energy source is a reality.

Photochemical Methods

Many impurities can be removed from solutions by means of sorption /106
methods. However, such compounds as alcohols, ketones and many other compounds, when they occur in large concentrations, are practically impossible to absorb with activated charcoal and ion-exchange resins. New methods are required to eliminate them.

One such method is the method of photochemical chlorination or oxidation. It is well known that chlorine is capable of replacing hydrogen in the hydrocarbon chain of organic substances (Varshavskiy, 1960). The chlorine derivatives of organic compounds which are thus formed, in view of general theoretical considerations, must be much more easily absorbed by activated charcoal. This reaction proceeds much more easily in the case of carbon atoms which are bound with such activating groups as the carbonyl and carboxyl groups. It is still easier to join chlorine with double carbon-carbon bonds with the formation of dichloro derivatives which are also more easily absorbed than the original unlimited compounds. In addition, the hypochlorous acid which is formed in the course of the hydrolysis of chlorine in aqueous solutions is a very strong oxidizer.

At room temperature, chlorination takes place at a slow rate. However, the chlorination reaction of the hydrocarbon chain is a radical process and consequently may be accelerated considerably under the influence of ultraviolet light (Semenov, 1937). Sources of ultraviolet radiation are well known (for example, PRK-7, SVD-120, BUV and others) and they are characterized by low energy requirements. In addition, it is possible under spaceflight conditions to use the ultraviolet component of the solar spectrum.

Another possible photochemical method is the irradiation of aqueous solutions with ultraviolet light when these solutions have been treated with small amounts of hydrogen peroxide. We can expect that when such compounds as alcohols, ketones and other low members of the homologous series of organic substances containing oxygen are oxidized, acids, aldehydes and carbon dioxide can be obtained. The most preferred version is total breakdown of the im- /107
purities to form $CO_2$ and $H_2O$.

The use of $H_2O_2$ as an oxidizer has a number of advantages over chlorine. When hydrogen peroxide is decomposed, water and oxygen are formed; hydrogen peroxide is easily dispensed and the excess $H_2O_2$ can be broken down easily with metallic catalysts or AV-17 anionite.

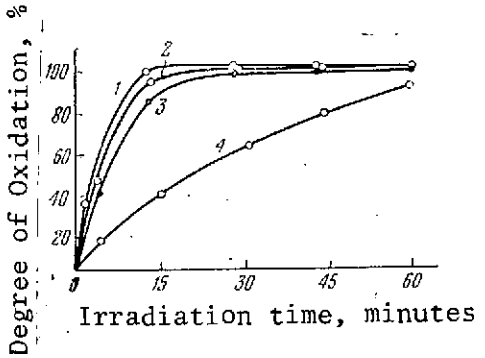



Figure 28. Change in the Degree of Oxidation of Alcohols and Acetone as a Function of Irradiation Time.
1, n-butanol; 2, Ethanol;
3, Methanol; 4, Acetone.

Figure 28 shows the changes in the degree of oxidation of alcohols and acetone as a function of irradiation time for concentrations of organic impurities of 50 mg/liter and hydrogen peroxide of 160 mg/liter. We can see from the figure that even a 15-minute exposure causes considerable oxidation of alcohols (80-90%); as a result of a 30-minute exposure, there is 100° oxidation of n-butanol, ethanol and methyl alcohol, and 60% oxidation of acetone. The results were obtained by means of a laboratory system whose external appearance is shown in Figure 29.

Irradiation of aqueous solutions of these compounds for 60 minutes causes practically complete oxidation of acetone. With equal molar concentrations of organic impurities, the latter are oxidized by hydrogen peroxide to various degrees and can be arranged in /108
the following order in terms of their capacity for photochemical oxidation:

n-butanol -- ethanol -- methanol -- acetone.

As a result of the photochemical oxidation of organic compounds, a gaseous phase is formed at the rate of 50 ml/liter of irradiated solution. According to data from chromatographic analysis, the gas mixture is composed of 80.8% oxygen, 17.6% nitrogen and 1.6% carbon dioxide. The development of the carbon dioxide is evidently caused by the extensive oxidation of the organic impurities, most of which are transformed into acids.

Hence, by using the method of photochemical oxidation, it is possible to get rid of such compounds as alcohols and ketones which are practically not absorbed by sorbents and to create a water regenerating system that is characterized by comparatively low energy consumption.

## Crystal Hydrate Method

The essence of the crystal hydrate method consists in the formation of hydrates in the processing of solutions of certain organic compounds (Donath, 1959; Williams, 1961, 1964; Medvedev, 1964). Hydrates are salt-free crystals with the formula $OC \cdot nH_2O$ where OC stands for organic compound; a light

hydrocarbon or its halide derivative. Such compounds as propane, freons ($CH_2FCl$, $CHCl_2F$), methyl bromide and several others are most widely used in purification systems. After separating the crystal hydrates from the concentrate, they are rinsed with fresh water; after the mother liquor of the brine is removed and subsequent dilution is carried out, salt-free water is obtained.

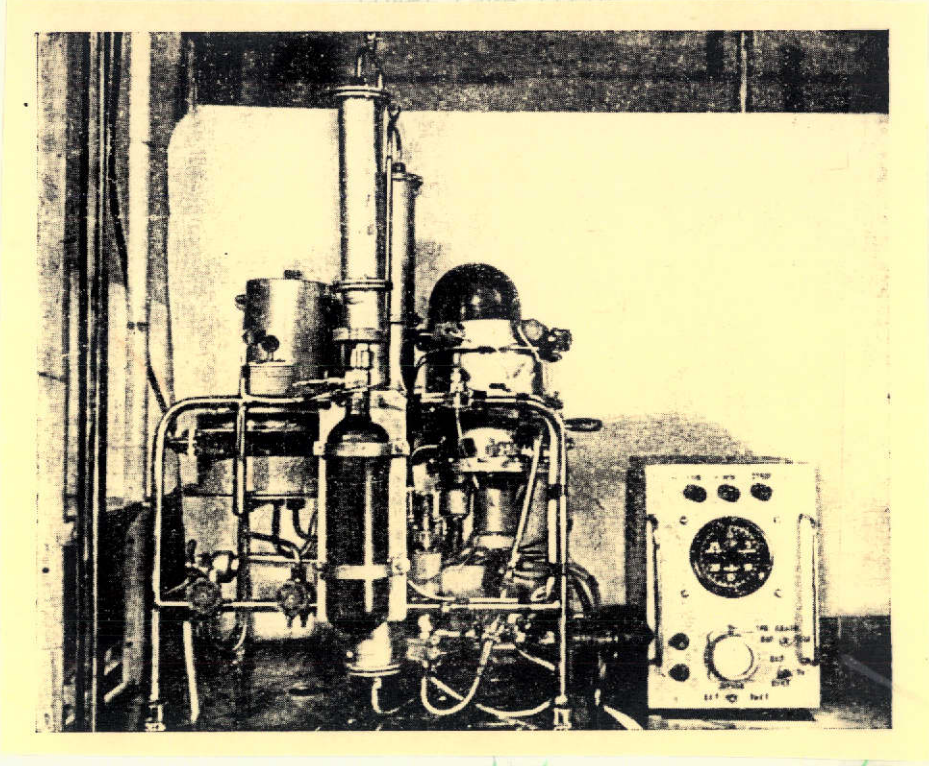


Figure 29. External View of a Laboratory System for Regeneration of Water by the Photochemical Method.

The crystal hydrate method is considered to be potentially feasible, since it has a number of advantages over other methods. Thus, the temperature of the process, depending on the nature of the hydrate-forming compound, is 3-25°, making it possible to use the heat given off by instruments and equipment in the spacecraft cabin. The pressures used are also low and vary from 1-3 atm.

In addition to the apparent advantages of the crystal hydrate method, there are a number of shortcomings which limit its use for extraction of water from waste products which contain both inorganic and organic impurities. Thus, when a portion of the water is extracted the concentration of the salts and organic compounds will increase, leading to contamination of the hydrates. This phenomenon is not observed when marine water is converted to fresh water, since in this case the concentration of the original product remains practically constant. Moreover, the intercrystalline space becomes filled with brine, which must be removed by a stage involving rinsing of the crystal hydrates with pure water. This stage considerably reduces the degree of extraction of the water. Increasing the pressure promotes an improvement in

the formation of hydrates leading to an increase in energy consumption. /109
Necessary additional purification to get rid of residual impurities and gas reagent likewise reduces the value of the crystal hydrate method.

Regeneration of Water by the Extraction Method

The essence of the extraction process consists in the conversion of the material being extracted from one phase (liquid or solid) to the phase of the liquid extractant with mutual contact between them. In terms of spaceflight conditions the extraction method has a number of advantages: 1) low working temperatures, 2) possibility of extracting impurities from dilute solutions, 3) possibility of separating mixtures composed of components with similar boiling points, including azeotropic impurities, 4) simplicity of apparatus.

Inasmuch as moisture-containing products of human vital activity and wastes from biological and technical systems contain substances in various concentrations and differ markedly as to the spectra of the impurities, regeneration of the water can involve two versions of the extraction method: 1) extraction of impurities from aqueous solutions and 2) extraction of water from wastes.

It should be pointed out that the extractant to be used must possess the following characteristics: 1) selectivity, 2) ease of regeneration, 3) as great a difference as possible with respect to the original solution in terms of density, 4) slight volatility, 5) nontoxicity, 6) chemical inertness.

The higher aliphatic amines (Kolemen et al., 1961) and alkylphosphoric acids are most widely used as extractants for extracting impurities from solutions (Daymond, Tak, 1962).

The aliphatic amines are used for removing acids; alkylphosphoric acids are used for extracting calcium, potassium, sodium and other metals. Thus, Smith and Page (1963), using a 5% solution of methyldioctylamine achieved nearly complete extraction of chromic, hydrochloric, nitric, oxalic, succinic, sulfuric and phosphoric acid. With low initial acid concentration in aqueous solutions, neutral salts soluble in organic solvents are usually formed:

$$R_3N_{org} + HX_{aq} \rightleftarrows R_3NHX_{org},$$

where $R_3N$ is the amine and R is the hydrogen atom or some radical. Extraction of acids is increased as the energy of the acid-base interaction increases. At higher acid concentrations extraction is carried out by the salts of the amines above the stoichiometric ratio:

$$R_3NHX_{org} + nHX_{org} \rightleftarrows R_3N(HX)n_{org}.$$

In this case extraction of the acids increases as their degree of dissociation decreases.

The extraction method has been used for the extraction of impurities from a condensate of atmospheric moisture (Khomchenko, Chizhov, Sinyak, Krasnoshchekov et al., 1971). Mineral and carbonic acids (HCL, $H_2SO_4$, $HNO_3$, $CH_3COOH$) were extracted by means of tri-n-octylamine; potassium, sodium and ammonium hydroxide were extracted with di-2-ethylhexylphosphoric acid. Extractions of acids by tri-n-octylamine was carried out using a condensate of atmospheric moisture that was passed through KU-2 cationite in the $H^+$-form. Extraction of the potassium, sodium and ammonium ions was accomplished using a solution that had been treated previously with AV-17 anionite in the $OH^-$-form. The results of the use of the extraction method for water regeneration from a condensate of atmospheric moisture are shown in Table 22. /110

TABLE 22.* RESULTS OF EXTRACTION OF CERTAIN COMPOUNDS FROM A CONDENSATE OF ATMOSPHERIC MOISTURE BY TRI-n-OCTYLAMINE AND DI-2-ETHYLHEXYLPHOSPHORIC ACID

| Components of the condensate | Concentration of impurities, mg/liter | | | |
|---|---|---|---|---|
| | Following passage through KU-2 H | | Following passage through AV-17 OH | |
| | 1 | 2 | 1 | 2 |
| HCl | 7,2 | 0 | — | — |
| $H_2SO_4$ | 7,35 | 0 | — | — |
| $CH_3COOH$ | 18,0 | 0 | — | — |
| $HNO_3$ | 0,05 | 0 | — | — |
| $HNO_2$ | 0,05 | 0 | — | — |
| NaOH | — | — | 13,2 | 0 |
| KOH | — | — | 13,5 | 0 |
| $NH_4OH$ | — | — | 11,5 | 0 |
| Alcohols | 10 | 10 | 10 | 10 |
| Aldehydes | 8 | 8 | 8 | 3 |

Note: 1, before extraction; 2, after extraction.

*Note: Commas indicate decimal points.

As we can see from Table 22, tri-n-octylamine and di-2-ethylhexylphosphoric acid allow total purification of condensates of atmospheric moisture to remove acids and alkalis.

Regardless of the extremely low energy expenditures required for performing the extraction process, the version described above has a number of shortcomings. Thus, for example, such compounds as alcohols are practically not extracted at all. So far the problem of regeneration of the extractant has not been solved. In addition, the operations involved in converting the salts to acids and bases are comparatively inconvenient. The method of extraction of water from the solutions would seem to be more feasible.

It has been pointed out that some organic compounds dissolve at low temperature in a larger amount of water than at high temperatures. Davison and Hood (1963), as a result of studying 400 organic substances, found that /111

compounds which contain one or more electrically negative atoms (such as oxygen or nitrogen) are capable of forming hydrogen bonds with water molecules and consequently possess the ability to extract water from solutions.

Low-molecular amines have proven to be the most effective extractants for obtaining fresh water from sea water. Using triethylamine as an extractant for removing water from urine, Khomchenko, Chizhov, Sinyak, Krasnoshchekov and others (1971) have shown that the phase diagram of the triethylamine-water system is characterized by a low critical stratification temperature of 18.7°; in the case of the triethylamine-urine system this value is displaced 10-15° to a region of lower temperatures.

The system for regeneration of water from urine, based on the extraction method, includes (Figure 30) coolers for reducing the temperature to levels that will allow the most complete extraction of the water; an extraction column which is necessary for mixing the extractant and the wastes; a heater which raises the temperature up to the stratification limits of the solution; a separator for regenerating the extractant and separating the pure water; an adsorber which makes it possible to carry out a high degree of purification of the water to remove the extractant and impurities from the wastes.

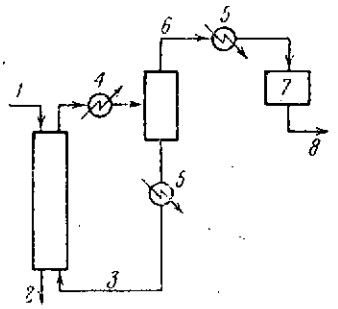



Figure 30. Diagram of a System for Regenerating Water by the Extraction Method.
1, Pipe for wastes; 2, Concentrator; 3, Extractant; 4, Heater; 5, Coolers; 6, Pipe for regenerated water; 7, Adsorber with activated charcoal; 8, Pipe for drinking water.

An important advantage of the extraction method is the high temperature of extraction and regeneration of the extractant. However, the feasibility of this method is reduced by the possibility of contamination of the cabin air by organic solvents as well as by the need for using the force of gravity (natural or artificial) to separate the solution. It is impossible to use the extraction method under weightless conditions.

Freezing-Out Method

The method of purifying water by freezing out is based on the effect of lowering the freezing point of solutions relative to pure water. When salt solutions are cooled, ice crystals initially form which are impoverished with respect to impurities. By removing the ice crystals from the solution and subsequently thawing them, then subjecting them to repeated freezing, a large part of the salts can be removed. Devices based on the freezing-out method can take three forms: 1) using refrigerators with a heat-transmitting surface; 2) extraction of heat by boiling fluids (freon, hydrocarbons, etc.), 3) extraction of heat from vaporization under vacuum conditions. /112

The latter two versions are obviously difficult to achieve under weightless conditions. Use of freons or hydrocarbons as freezing agents, added directly to the solution to be purified, assume the use of a rotating ice generator. When using evaporation from a portion of the water in a vacuum, there will be a considerable loss of moisture in the heat-removal process if the vacuum of space is used.

The first version is by far the more preferable. At the present time we know a number of ways of building desalination devices which operate on the freezing-out principle. A diagram of one of them is shown in Figure 31 (Kerran, 1963). The water to be purified enters ice generator 3, where it is cooled by a coolant supplied by refrigerator 4. When the water freezes under continuous mixing conditions, fine ice crystals are formed which fall onto conveyor belt 6 and enter thawing chamber 8. Some of the ice thaws above the brine collector 2, washing the ice out of the brine. Most of the fresh ice thaws above the fresh water collector 10, with a jet of air directed on the ice by fan 9. In all, about 0.2 $m^3$ of fresh water containing 0.5 grams of salt per liter can be obtained from 1 $m^3$ of water with a salt content of 32 g/liter.

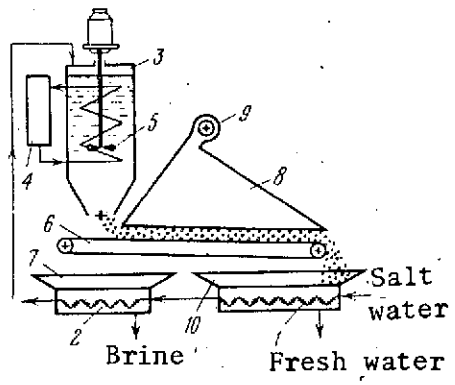



Figure 31. Diagram of a Device for Purifying Water by the Freezing-Out Method (According to Kerran, 1963).
1,2, Heat exchangers; 3, Ice generator; 4, Refrigerator; 5, Mixer; 6, Conveyor belt; 7, Brine collector; 8, Ice--thawing chamber; 9, Fan; 10, Fresh water collector.

The freezing-out method has a number of shortcomings in conjunction with water supply systems, one of which is the low degree of water extraction. In addition, the organic non-distilling compounds, which change the freezing point of the solution insignificantly, will enter the composition of the ice crystals or will be adsorbed on their surfaces, thereby contaminating the fresh water which is produced. Hence, an additional sorption purification unit is required. /113

One of the versions of the freezing-out method is the purification of water by zone freezing of the solution (Mink et al., 1963). This method assumes local ice formation with subsequent mixing of the freezing zone along a vertical pipe filled with water to be purified. A layer of water with an increased salt concentration, bounded by ice crystals, moves into the vicinity of a solution with low impurity concentrations. The ice which is formed melts under the influence of the heat contained in the new batch of solution to be purified when the latter enters the inlet of the purification system.

The advantages of this version of the water purification method as far as spaceflight conditions are concerned consist in the use of low temperatures for carrying out the process, thus sharply reducing the vital activity of microorganisms. Moreover, it is possible to use the cold on the non-illuminated side of the spacecraft. However, as in the ordinary freezing-out method, the degree of extraction of water from waste products is clearly not very high and requires additional regeneration methods.

## Other Methods of Water Regeneration

### Method of Wet Combustion

The essence of the method of wet combustion consists in the oxidation of products of human vital activity and waste products from biological systems in acids, alkalies or by means of oxygen in the liquid phase (water) at high pressures (Able, Morgan, Rouf, 1954; Zimmerman, 1958; Simpson, 1962; Drigo, Sinyak et al., 1967). As far as the regeneration of water is concerned, use of the wet combustion method employing acids or alkalies poses considerable difficulties since it involves the consumption of aggressive reagents and their production.

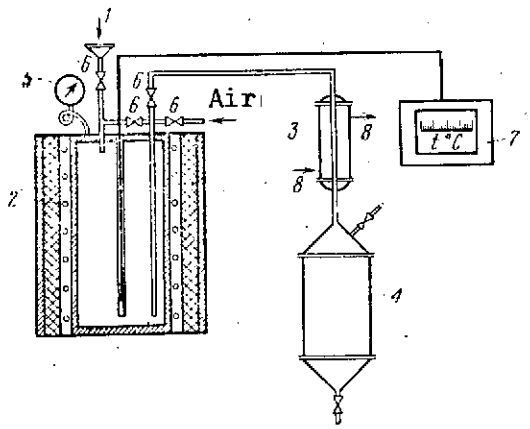



Figure 32. Diagram of a Device for Oxidation of Products of Human Vital Activity by the Method of Wet Combustion.
1, Funnel for wastes; 2, Autoclave; 3, Condenser; 4, Receptacle; 5, Manometer; 6, Valves; 7, Thermograph; 8, Inlet and outlet for coolant.

However, the first efforts at the use of the wet combustion method using oxygen (in the pure form or mixed with nitrogen) at high pressures showed that at 200-300° and pressures of 50-150 atm the organic components of tap water are oxidized 80%. The gas medium which is formed consists primarily of carbon dioxide and molecular nitrogen with a small amount of saturated hydrocarbons and hydrogen. The liquid phase contains dissolved salts and there is also a precipitation of a small amount of residue. In conjunction with spaceflight conditions, the method of wet combustion was studied by Drigo, Sinyak et al. (1967). To study the process of oxidation at high pressures and temperatures the authors used the device which is shown in Figure 32.

Homogenized products of vital activity enter autoclave (2), with a capacity of 1 liter, through funnel (1). The oxygen in the air is used as the oxidizer; the air is pumped into the autoclave up to a certain pressure through a valve. By means of an electrical heater in the autoclave, the temperature and pressure are increased to levels required for accomplishing /114

the oxidation reaction. The solution which is obtained as a result of wet combustion passes through the valve into the condenser (3) and receptacle (4).

To determine the effectiveness of the wet combustion process both the raw materials and the end products are analyzed as follows: the quantity of organic substances is determined on the basis of bichromate oxidability, the organic nitrogen is determined by the Kjeldahl method, the nitrogen from nitrites by the Griss method, the nitrogen from nitrates by the sulfosalicylic or sulfophenol method, with subsequent colorimetry on the FEK-M, and the nitrogen in the ammonia by colorimetry using Nessler reagent. The potassium and sodium ions were determined using the method of flame photometry. The calcium concentration was measured complexometrically using trylon B at pH 12 in the presence of an indicator (dark-blue chromium). The iron content was determined in an alkaline medium using sulfosalicylic acid with subsequent colorimetry. The measurements of the phosphorous content were performed using ammonium molybdate with subsequent colorimetry and parallel titrometry using lanthanum nitrate. The chlorides were determined using the Folgart method with silver nitrate. An analysis of the gas medium was performed using the volumetric method by means of the VTI gas analyzer.

The first series of experiments was performed with high levels for the parameters of the process: temperature of 300° and an initial air pressure in the autoclave of 50 atm. The mixture of urine and feces that was autoclaved was composed of 75-150 ml of urine, 20-40 g of feces and 500 ml of water. The results of the mineralization experiments, performed under these conditions, /115
are shown in Table 23. For comparison, we have included in the table the chemical composition of standard nutrient solutions used for the cultivation of lower plants (Tamiy medium) and higher plants (Knop medium).

As we can see, the efficiency of oxidation in this version of the experiment is 92-93%. The solution which is obtained as a result of wet combustion is a clear liquid. The solution of urine and feces disappears and there remains only a slight odor of an unspecific nature. When the solution is allowed to stand, a white precipitate settles out. An interesting property of the mineralized solution is the occurrence of nitrogen in the liquid form as ammonia.

The gas phase, obtained as a result of mineralization of mixtures of urine and feces by the wet combustion method, consists primarily of nitrogen, carbon dioxide and residual oxygen. The concentrations of carbon monoxide and hydrogen sulfide are beyond the limits of sensitivity of the volumetric method. However, in the gas phase one can detect the presence of a small amount of /116
saturated hydrocarbons and hydrogen. The composition is given below (in volume %):

| | | | |
|---|---|---|---|
| $CO_2$ | 6-7 | CO | Not observed |
| $O_2$ | 8-13 | $H_2$ | Not observed |
| $N_2$ | 79-80 | Saturated hydrocarbons | 0.3-0.7 |
| $H_2$ | 0.5-0.7 | | |

TABLE 23. CHEMICAL COMPOSITION OF MINERALIZED SOLUTIONS OF URINE AND FECES AND STANDARD NUTRIENT SOLUTIONS

| Component Elements and Parameters, mg/l | Mineralized Solution | Medium | |
|---|---|---|---|
| | | Knopa | Tamiya |
| Nitrogen | | | |
| general | 1,700 | 153.3 | 700 |
| ammonia | 1,600 | 0 | 0 |
| nitrates | 1 | 153.3 | 700 |
| nitrites | 0 | 0 | 0 |
| Potassium | 390 | 168 | 2,250 |
| Phosphorus | 32 | 57.0 | 285 |
| Calcium | 18 | 169.5 | 0 |
| Iron | 2-3 | 1.2 | 3 |
| Chlorides | 2,000 | 2.2 | 0 |
| Magnesium | 18-24 | 24.7 | 240 |
| Sulphur | 660 | 32.4 | 320 |
| Original oxidizability, mg $O_2$/l | 20,000-50,000 | -- | -- |
| Final oxidizability, mg $O_2$/l | 1,400-4,000 | -- | -- |
| pH | 6.3-9.2 | -- | -- |
| a*, % | 92-93 | -- | -- |

*a = the coefficient of oxidation calculated by the formula:

$$a = \frac{A_{org} - A_{final}}{A_{org}} \cdot 100,$$

where $A_{org}$ is the amount of organic substance in the original solution, and $A_{final}$ is the final amount of organic substance which remains after oxidation.

Under actual flight conditions, the existence of this process at reduced temperatures and pressures acquires a certain degree of significance. Experiments performed for this purpose have shown the possibility of oxidation of the products of vital activity with a considerable decrease in these parameters. Figure 33 shows the results of oxidation of mixtures of urine and feces at two temperature levels (220 and 320°) and various pressure regimes in the autoclave during combustion (initial pressure in both versions was 10 atm while the final pressure was 25 and 80 atm, respectively).

As we can see, in this version of the experiment 70-80% oxidation could be achieved. The nature of the curves obtained indicates that the process of conversion of mixtures of urine and feces by the method of wet combustion is characterized by high rates of combustion during the first hours of the process and insignificant increase later on.

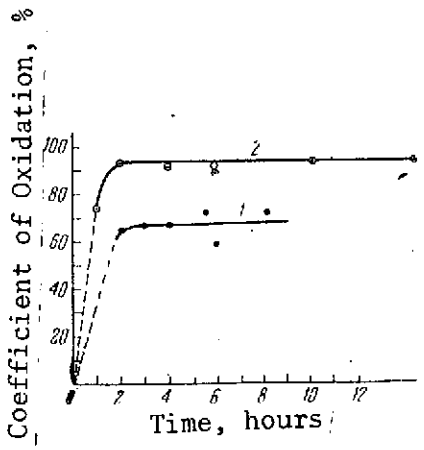



Figure 33. Coefficient of Oxidation (α) of the Organic Component of Human Vital Activity Products Versus the Duration and Temperature of the Combustion Process. 1, Temperature 220°, initial pressure 10 atm, final pressure 25 atm; 2, Temperature 320°, initial pressure 10 atm, final pressure 80 atm.

The solution obtained as the result of processing of human vital activity products by the wet combustion method is characterized by high pH values (approximately 9). This is due to the liberation of ammonia in the hydrolysis of urea, which leads to alkalinization of the medium and the precipitation of calcium and magnesium phosphates.

Most of the organic compounds are oxidized to form $CO_2$, $H_2O$ and other oxides. However, the solution which is obtained must be subjected to additional purification: the mineral part, for example, is refined by means of electrodialysis and evaporation, while the organic compounds are treated by one of the oxidation methods, for example a catalytic method. Thus, Yagow et al. (Yagow, Yaffe, Saunder, 1970), by using nickel, ruthenium and platinum catalysts, succeeded in oxidizing mixtures of urine and feces up to 99.2%: the amount of nitrogen from ammonia was 3.6 mg/g of waste and had a pH of 8.4.

The wet combustion method can be used to regenerate water from all human vital activity products as well as those from animals and plants. The solutions obtained are totally sterile, one of the advantages of this method. An interesting characteristic of this method of wet combustion is the possibility of building a regeneration device which operates independently on the energy obtained from moisture-containing waste products without having to add any energy from outside. /117

However, water regeneration systems that are based on the wet combustion method have a number of shortcomings as well. The principal obstacle to the use of this method on space flights is the need to work at high pressure. In this case, the probability of emergency situations is increased; consequently, there is a decrease in the reliability of the operation of the system. In addition, the non-oxidized portion of the organic compounds and the large amount of mineral salts in these solutions require the use of additional methods of regeneration.

## Ion-Osmotic Method

In 1958 Murphy described the ion-osmotic method of purification of water, which consists in transporting ions across a semipermeable membrane by diffusion of salts of different concentrations.

A diagram of the water purification process is shown in Figure 34. The ion-osmotic cell has several chambers separated by cation- and anion-permeable membranes. In the first stage of the process, the three central chambers are filled with saline water, while the first and last are filled with brine with a high salt concentration. Due to the difference in concentrations in the first and second chambers, diffusion of anions from the first chamber (containing the brine) into the second takes place. The cations cannot enter the second chamber, since the membrane separating the chambers is impermeable to cations. In the second chamber, this results in a reduced concentration of cations which will be offset by the cations that enter from the third (central) chamber, since the membrane which divides chambers 2 and 3 is permeable to cations. Similar processes occur in chambers 5, 4 and 3. In this case, the /118
cations from chamber 5 (brine) with a high salt concentration will diffuse into chamber 4, thereby creating a high concentration of anions in it. This is possible because the membrane which divides chambers 4 and 5 is impermeable to anions. Neutralization of the excess cations that pass into chamber 4 occurs by virtue of the anions that penetrate from chamber 3 (the central chamber), since chambers 3 and 4 are separated by a membrane which is permeable only to anions.

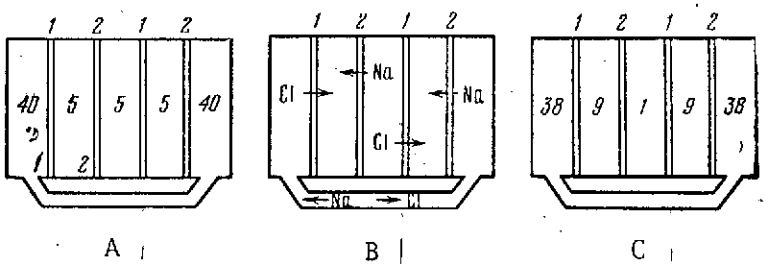



Figure 34. Diagram of Processes Aimed at Purification of Water by the Ion-Osmotic Method. a, Beginning of the process; b, Diffusion of anions and cations; c, End of the process. Numbers in the boxes: Concentration of NaCl solution (in g/liter); 1, Anode; 2, Cathode.

Hence, as the result of these processes the saline water in the central chamber will be purified. Inasmuch as the end chambers are connected by a pipe, excess cations and anions in chamber 1 are neutralized by circulating the solutions with a pump. The concentrations in chambers 2 and 4 are balanced in the same way.

Despite the obvious advantages of regeneration devices based on ion-osmotic methods (minimum energy expenditure, gentle conditions for carrying out the processes), it is obviously not possible to use them in water supply systems for spacecraft crews. The limiting factors in this respect are: the extremely low coefficient of extraction of water, the incompleteness of impurity extraction and the difficulty of getting rid of organic compounds (for example, urea).

Biological Methods

Purification of water in limited closed spaces may be carried out by means of biological methods employing microorganisms, unicellular algae and higher plants. Microorganisms are capable of accomplishing extensive breakdown of the most diverse organic compounds. By means of their enzyme systems, they can break these compounds down to form carbon dioxide, nitrates and sulfates.

The process of conversion of moisture-containing products of human vital activity by means of microorganisms is carried out either under aerobic conditions (with admission of oxygen) or under anaerobic conditions (in the absence of oxygen). Under aerobic conditions, the principal component of the waste products -- urea -- is broken down by urobacteria to form unstable carbon-ammonium salts, with subsequent breakdown into its components -- ammonia, carbon dioxide and water. Later, nitrogen-fixing bacteria may oxidize the ammonium salts to form nitrates, thereby completing the chain of microbiological conversion.

The microbiological breakdown to proteins (ammonium fixation) occurs most intensively under aerobic conditions, resulting in the formation of ammonia and organic acids of the aliphatic series, which then oxidize to form $CO_2$ and water.

Under natural conditions on Earth, microbiological processes involving the breakdown of organic compounds occur comparatively slowly and are subject to the influence of various environmental factors. However, if the oxidation process takes place under optimum conditions, the conversion rate can increase sharply. For this purpose, biofilters, air filters, "air tanks" and "methane tanks" (Lapshin, Stroganov, 1938; Botuk, 1949; Dolivo-Dobrovol'skiy, 1958; Bazyakina, 1958) are used. /119

The possibility of processing human vital activity products in conjunction with life-support systems for spacecraft crews was studied by V. F. Varlamov et al. (1967). They conducted three series of experiments. In the first two they processed wastes with an impurity concentration as determined by CCO (chemical consumption of oxygen) of 500 and 1,000 mg $O_2$/liter. The mixture was centrifuged to get rid of the roughly dispersed undissolved fractions of the feces. In the third series of experiments the mixture was treated with a concentration of wastes of 1,000 mg $O_2$/liter, with previously dispersed undissolved fecal fractions added to the solution. The studies were performed by means of an "air tank" -- a settling tank with the volume of the aeration section being 5.5 liters and the water column height equal to 120 cm. The weight ratio of the feces and urine was 1:2.

Table 24 shows the data which characterize the process of mineralization of waste products with respect to several nitrogen-containing substances. It has been established that in the course of 12 hours of aeration of fluid containing urine and feces mixed with activated sludge at temperatures of 18-20°, at a concentration of 500 mg $O_2$/liter according to CCO in the mixture and an

air flow of 0.9-1.0 liters/minute, there is approximately 90% decomposition of the organic compounds. However, this degree of oxidation was obtained by using /120 low concentrations of impurities, which made it necessary to dilute original mixtures with water up to 180-200 times. Increasing the concentration of the processed wastes up to 1,000 mg $O_2$/liter according to CCO, regardless of the improvement in the design of the "air tank", led only to 80% oxidation of the wastes.

TABLE 24. RESULTS OF BIOLOGICAL MINERALIZATION OF A MIXTURE OF URINE AND FECES WITH 12 HOURS EXPOSURE

| Parameters | Concentration of Mixture On The Basis of CCO*, mg $O_2$/liter | | | | | |
|---|---|---|---|---|---|---|
| | 500 | | | 1,000 | | |
| | Original Mixture | Mineralization | Activated Sludge | Original Mixture | Mineralization | Activated Sludge |
| CCO, mg $O_2$/liter | 500 | 52 | -- | 1,130 | 206.4 | -- |
| $NH_3$, mg/liter | 57 | 2.7 | -- | 100 | 35.6 | -- |
| $NO_2$, mg/liter | | 1.3 | -- | 0.07 | 1.47 | -- |
| $NO_3$, mg/liter | 0.5 | 35 | -- | 0.93 | 44.5 | -- |
| Dissolved $O_2$, mg/liter | -- | 5.25 | -- | -- | 3.7 | -- |
| pH | 7.0 | 6.5-6.8 | -- | 7.0-7.5 | 6.0-6.5 | -- |
| Dose of sludge used for mineralization, mg/liter | -- | -- | 240 | -- | -- | 121 |
| Dry weight of sludge, g/liter | -- | -- | 2.52 | -- | -- | 3.26 |
| Sludge index | -- | -- | 95 | -- | -- | 37.2 |

*CCO = Chemical Composition of Oxygen

The authors state that the original mixture of feces and urine, subjected to the above-described microbiological transformation, lost its specific odor and took on the stable odor of river water. The activated sludge, which made it possible to process the waste products, was in the form of compact, fine bacterial flakes which could easily be removed from the liquid. The solution also was found to contain ammonium-fixing bacteria up to $10^8$, nitrogen-fixing bacteria up to $10^7$ and denitrifiers of $10^3$-$10^5$/ml. In the process of oxidation of the wastes, a decrease in the number of E. coli bacteria was observed, from 21,000 to 580 bacteria per ml.

Hence, as a result of the microbiological processing of the wastes, it is possible to oxidize a considerable portion of the organic impurities. However,

such a solution is unsuitable for drinking purposes. In order to bring it up to generally accepted sanitary and hygienic standards it is necessary to get rid of the remaining organic compounds, mineral salts, etc., and to subject the solution to decontamination. These stages in purification, combined with the need for greater dilutions of water, considerably complicate the use of the microbiological method in water supply systems for spacecraft crews.

Obviously, the microbiological transformation of vital activity products from man will be effective when algal-bacterial mixtures are used or when higher plants are grown on media that are produced as the result of microbiological mineralization. In these cases, the problem of the regeneration system for water will amount to a purification of the condensates of the chlorella cultivators and greenhouses by these or other physical-chemical methods.

Obtaining Water on the Moon

Under lunar conditions, the water supply system of a spacecraft or lunar station may be designed to use the water or oxygen which is included in the composition of lunar minerals (Zwicky, 1961; Hendel, 1964; Rickles, 1964).

Thus, Zwicky states that lunar minerals similar to those on Earth may contain 1-10% water of crystallization. To extract it, solar generators may be employed which provide a temperature at the focus of more than 3,000°. The resultant steam can be used in turbines or (after a condensation stage) for drinking purposes and the cultivation of plants (Figure 35). In order to obtain oxygen and carbon dioxide it is necessary to use solar generators which provide temperatures of more than 4,000°. At this temperature, the calcium carbonates are dissociated to form CaO and $CO_2$. Carbon dioxide can be fed to a chlorella cultivator or subjected to thermal dissociation to form $O_2$ and CO. In the opinion of the authors, a solar generator that would have a reflector area of 0.8 $m^2$ would provide energy to obtain 264 liters of $O_2$/hour at atmospheric pressure as a result of dissociation of $CO_2$, $H_2O$ or any other oxide. This is sufficient for 15 men with an oxygen absorption rate of $O_2$ of approximately 15 liters/man/hour. A reflector with a diameter of 508 cm would make it possible to obtain 22 liters of water per day. Hendel (1961) states that lunar minerals may contain from 1 to 12% water which is chemically bound or in the form of crystals, which can be used for water supply systems. /122

In the opinion of R. Rickles (1964), the method of obtaining water on the Moon by means of a solar generator has some important disadvantages: it can only be used for the extraction of small amounts of water. In order to supply a lunar station with a population of 50 individuals with water, it will be necessary to devise new methods. If the lunar rocks are of volcanic origin, as the author suggests, they may contain 1 to 5% water; consequently, up to 4 liters of water can be obtained from 0.028 $m^3$ of rock. Lunar rocks can be dehydrated at t = 700-1,000° in a reactor with a pseudo-liquefied layer (Figure 36). In order to attain such temperatures, it is possible to use the

infrared portion of the solar spectrum. Infrared radiation, whose intensity is much higher on the Moon than on the Earth, may be concentrated and used for heating a heat conductor, a reactor, or a carrier gas. As the carrier gas, we can use nitrogen, steam or carbon dioxide. The hot gases can be used in a stream turbine to produce energy. The vapors can be condensed, in the author's opinion, by using the dark side of the Moon.

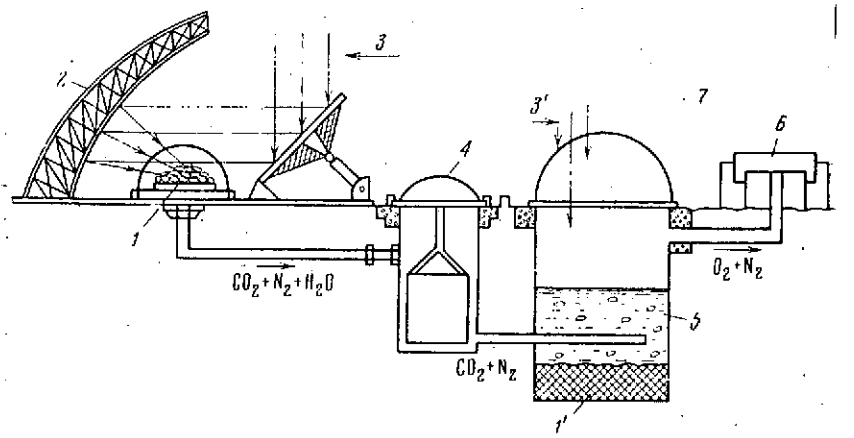



Figure 35. System for Producing Water, Oxygen, Nitrogen and Food on the Moon (According to Zwicky, 1961).
1, Lunar soil; 2, Reflector; 3, Sunlight; 4, Condensed water; 5, Chlorella cultivator; 6, Oxygen; 7, Vacuum.

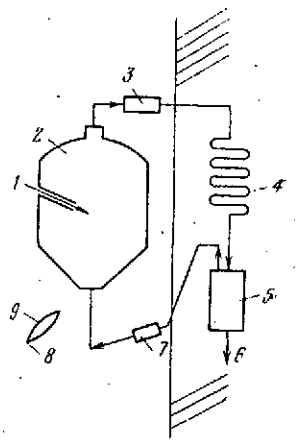



Figure 36. Diagram of a Device for Dehydration of Lunar Rocks (According to Rickles, 1964).
1, Lunar rocks; 2, Pseudo-liquefied layer; 3, Steam turbine; 4, Cooler; 5, Condenser; 6, Water; 7, Air; 8, Lens; 9, Sunlight.

The second theoretically different process for obtaining water under lunar conditions is the reduction of oxides which form part of the lunar rocks, using reducers. The reduction process can be accomplished at $t \approx 800°$ (Rickles, 1964).

One of the possible sources of energy for obtaining water from lunar minerals is a nuclear reactor which provides temperatures above 3,000°. In this case, it is possible either to use directly the thermal energy given off in a nuclear reactor, or electrical energy. With a sufficient amount of electrical energy available, the use of lasers may be attempted (Figure 37).

One of the numerous problems that arise in conjunction with obtaining water under lunar conditions is the transportation of the rock from a vacuum (more than $10^{-13}$ mm Hg) to a chamber with a pressure of $0.5 \pm 1.0$ atm, unloading the processed rock

from the chamber into the vacuum. According to the data of Soviet researchers (Vinogradov, 1972) who have analyzed the lunar rocks that were brought back by the Luna-16 and Luna-20 spacecraft (from the northeastern part of Mare Fecunditatis and the high-mountain region of the crater Apollonius-S), lunar soil consists primarily of silicon, aluminum, iron, calcium and titanium oxides (Table 25). /123

TABLE 25. CHEMICAL COMPOSITION OF LUNAR SOIL RETURNED TO EARTH BY "LUNA-16" AND "LUNA-20"

| Oxides | Crystallized Rock | | Soil | |
|---|---|---|---|---|
| | Basalt, Luna-16 | Anorthosite Type with Olivine, Luna-20 | Regolith, Luna-16 | Regolith, Luna-20 |
| Silicon | 42.95 | 42.40 | 41.90 | 44.40 |
| Aluminum | 13.88 | 20.20 | 15.33 | 22.90 |
| Iron | 20.17 | 6.40 | 16.66 | 7.03 |
| Calcium | 10.80 | 18.60 | 12.53 | 15.20 |
| Magnesium | 6.05 | 12.00 | 8.78 | 9.70 |
| Titanium | 5.50 | 0.38 | 3.36 | 0.56 |
| Sodium | 0.23 | 0.40 | 0.34 | 0.55 |
| Potassium | 0.16 | 0.52 | 0.10 | 0.10 |

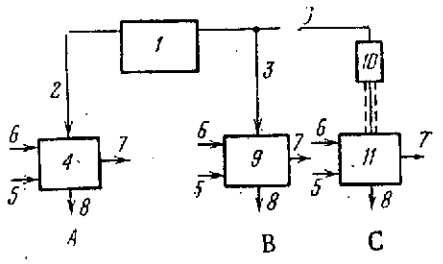



Figure 37. Diagram of a Method of Obtaining Water and Oxygen From Lunar Silicates.
1, Nuclear reactor; A. System for obtaining water by using thermal energy; 2, Heat supply; 4, Thermal reactor; 5, Conveyor for lunar soil; 6, Supply of reducer; 7, Silicon oxide ($SiO_2$) conveyor; 8, Output for water and oxygen; B, System for obtaining water by using a plasmotron (9); 3, Input of electrical energy; C, System for obtaining water using a laser (10); 11, Reactor.

By using certain gases, for example hydrogen, we can reduce the above oxides to form water. Some of the water which is obtained can be used for drinking while some can be broken down by electrolysis to form oxygen and hydrogen. The oxygen can be used for breathing or as fuel while the hydrogen can be used again for reducing the oxides.

The studies of workers at the California Institute of Technology have shown that samples of lunar rock returned to Earth by the crews of the Apollo-11 and -12 spacecraft contain $2 \cdot 10^{-3}$% water. It must be emphasized that on Earth the "driest" rocks contain 1-2% water. It is true that the workers at the NASA Manned Spacecraft Center found traces of three minerals in the lunar rock samples: mica, amphibolite and aragonite, which contain 1-2% water under terrestrial

conditions. Therefore, we cannot exclude the possibility that the deeper layers of the Moon may contain rocks which resemble terrestrial ones as far as the amount of water they contain is concerned. In this case, the technology for obtaining the water is very simple and will involve processes of heating the rock to dehydrate it and subsequently condensing the water vapor. Since impurities will enter the condensate (possibly compounds of a sulfurous nature), additional purification will be required to obtain drinking water or water for technical needs, using sorption or other physical and chemical methods.

Despite the presence of water in lunar rocks, 10 researchers at the NASA Manned Spacecraft Center in Houston have patented a method and a device for /124
obtaining water and its component elements (hydrogen and oxygen) from lunar soil, based on the fact that the samples of lunar material collected by the Apollo-11 and -12 expeditions contained considerable amounts of the iron--titanium oxide known as ilmenite.

The method is based on the chemical process of reduction of the iron oxides by means of hydrogen and solar energy for the purpose of obtaining water vapor which can be broken down by electrolysis to form oxygen and hydrogen. The device described in the patent involves a reflector for focusing the Sun's rays on a container of lunar soil, heating it to 600-1,300°. As soon as the temperature of the soil reaches the required level, hydrogen is admitted to the reactor to form steam with the oxygen atoms in the ilmenite. The resultant steam passes through an electrolysis cell where the water is decomposed to form oxygen and hydrogen. The hydrogen used in the reaction must initially be obtained from Earth; in subsequent cycles it will be regenerated in the electrolysis cell.

The chemical process has been tested in the laboratories at the Manned Spacecraft Center, where substances simulating lunar rock were used. The imitation rocks were obtained by mixing appropriate proportions of basalt from the Hawaiian Islands and ilmenite from Canada.

Calculations have shown that the hydrogen process can be used to obtain 1 kg of water from 100 kg of lunar rock. However, if the iron oxides are concentrated by a magnetic method, the output rises to 14%.

In addition to hydrogen, other chemical reagents have been discussed. For example, fluorine gives a much greater oxygen output but requires the use of a more complicated technological process and equipment. Moreover, when fluorine is used the water cannot be used directly, and oxygen is given off.

The hydrogen and fluorine methods of obtaining oxygen and water from lunar soil are being studied at the Manned Spacecraft Center in Houston and the Lewis Research Center in Cleveland. Information on technological developments in processes of obtaining water from lunar minerals is lacking in the literature.

## Selection of Systems for Regeneration of Water for Space Flights of Varying Duration

The choice of a water regeneration system for a specific spacecraft is a function of a number of factors. These include the following:

- minimum equivalent (applied) weight,
- maximum reliability,
- high degree of water extraction,
- simplicity of operation, /125
- possibility of functioning under weightless conditions,
- impossibility of spreading toxic compounds into the environment,
- low noise level,
- degree of processing, etc.

The equivalent (applied) weight, which includes the weight of the basic equipment of the system, the weight of the energy supply sources, spare parts, materials and substances to be used, etc., gives a good idea of the feasibility of using a given method of regeneration in comparison with a water supply system based on reserves.

For example, let us look at NASA data for a 500-day flight by a 9-man crew with an equivalent weight for the water regeneration system based on the evaporation of waste products in a stream of air (with a closed cycle). Figure 38 shows the diagram (and Table 26 gives the equivalent weight) of a system for producing 5.6 kg/hour, operating 18 hours a day, as proposed by NASA.

Fluid wastes accumulate in the preprocessing containers (2), from which a /126
mixture of chromium trioxide and sulphuric acid enters from a tank containing chemical reagent (5), so that the free amonia is chemically bound and the bacteria are destroyed. Two containers are used: the waste products enter one of them and waste products are simultaneously dispensed from the other by means of pump (8) into evaporating container (11). The water is evaporated into a stream of circulating carrier gas passing over the container. The carrier gas may be the same as the air in the pressurized cabin, or it may be different. In any case, the carrier gas removes the water from the container and brings the evaporator to a state which is near saturation and has a reduced temperature. Then it enters the condenser-separator (12) where the vapor is condensed and separated from the gas, which returns to the evaporator, passing through the heater on the way (22).

The condensate is continuously removed and passed through carbon and bacterial filters. If one of the two conductometric sensors (15) indicates unsatisfactory water quality, the flow is automatically diverted into the urine receptacle. At the same time, the supply valve to the input of the bacterial filter (16) closes and a preliminary emergency signal is given to indicate that necessary repairs must be made.

When one of the preprocessing containers is empty, the supply valve automatically shuts it off, connecting the second container, so that the process

goes on continuously. At the same time, a new batch of waste products is transferred to the empty container. Two evaporators (11) are provided for this purpose: one is on the main line and the other is on a bypass. The exhausted material in the bypass evaporator can be sterilized with steam, dried /127 and subjected to a vacuum in deep space prior to being removed. This procedure saves the crew any unpleasantness associated with cleaning the container.

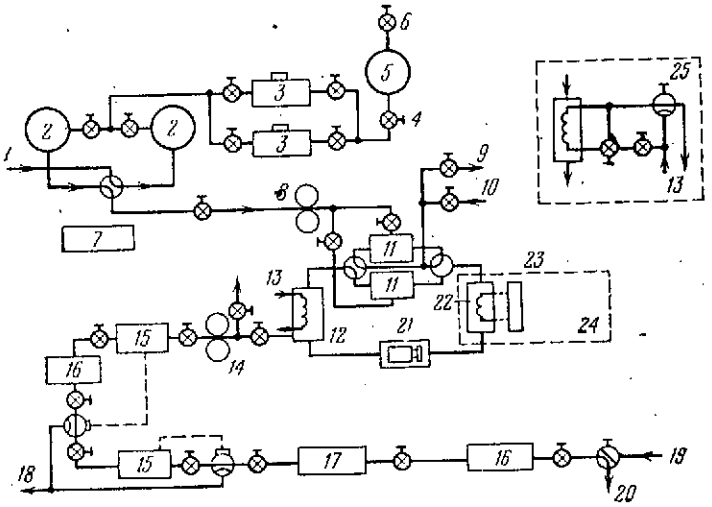



Figure 38. Diagram of a System for Regeneration of Water, Based on the Method of Evaporation in an Air Stream.
1, Input for liquid waste; 2, Waste collector; 3, Injector; 4, Valve-separator; 5, Tank of chemical reagents; 6, Valve; 7, Control panel; 8, 14, Pumps; 9, Valve leading to space; 10, Steam line; 11, Wick evaporator; 12, Condenser-separator; 13, Coolant; 15, Conductometric sensors; 16, Bacterial filter; 17, Layer of activated charcoal; 18, Output to urine receiver; 19, Steam; 20, To drinking water container; 21, Fan; 22, Heater; 23, Thermostat; 24, Diagram of N1 heat exchanger; 25, Diagram of heat exchangers.

In order to have complete equipment for the water regeneration system described above it is necessary to have the following reserve elements and supplementary equipment (for example): evaporator 1; tank of chemical reagents 1; thermal evaporator 1; condenser-separator 6; distributor valve 1; fans 2; cartridge of activated charcoal 1; pumps-dispensers 3; four-way solenoid valves 2; three-way solenoid valves 2; injector for supplying chemical reagent 1; four-way distributor valve 1; supply valves 2; feedback valve 1; conductometric sensors 3; cartridge with bacterial filter 1; heater regulators 2; control blocks 2; water pumps 3; heater 1.

TABLE 26. EQUIVALENT WEIGHT (in kg) OF WATER REGENERATION SYSTEMS BASED ON EVAPORATION IN A STREAM OF AIR (PRODUCTIVITY OF 5.6 kg/hr) AS A FUNCTION OF THE ENERGY SUPPLY SOURCE

| Components of the System | Source of Electrical Energy | | |
|---|---|---|---|
| | Solar Batteries | Solar Batteries + Isotope source | Energy source, Brayton cycle |
| Basic equipment | 327 | 327 | 327 |
| Reserve elements and additional equipment | 136 | 136 | 136 |
| Electrical energy source | 884 | 9 | 9 |
| Thermal energy source | --- | --- | --- |
| Weight of radiator | 268 | 268 | 268 |
| Total equivalent weight | 1,615 | 740 | 740 |

As we can see from Table 26, the total equivalent weight of the regeneration system is 740 to 1,615 kg depending on the type of energy supply source. The peak power of version No. 1 is 4,340 watts with a volume of 2.12 $m^3$. The planned service life is 200 hours per flight, with the average time of non-emergency operation being 20,000 hours. In view of the 37 additional parts, the total calculated reliability of the system is 0.999447. The data in the table indicate that the maximum mass in the water regeneration system is concentrated in the electrical power supply. The use of isotope heat sources will make it possible to cut down the equivalent weight significantly.

Hence, a regeneration system with an equivalent weight of 740 kg makes it possible to regenerate 50,000 kg of water during the flight. If we consider the weight of the containers for storing this amount of water, the advantages of the water supply system based on regeneration processes become particularly clear.

As calculations have shown, the equivalent weights of many physical-chemical water regeneration systems are very similar. In the following we have listed the minimum equivalent weights of the regeneration system for providing water to a crew of 9 men on a 500 day voyage.

| Method | Equivalent Weight of Regeneration System, kg |
|---|---|
| Vacuum distillation - steam compression | 738 |
| Vacuum distillation - thermoelectric effect | 679 |
| Vacuum distillation - pyrolysis (catalytic oxidation) | 808 |
| Flash evaporation - pyrolysis | 801 |
| Flash evaporation - steam compression - pyrolysis | 833 |
| Evaporation in a flow of air (open cycle) | 710 |
| Evaporation in a flow of air (closed cycle) | 740 |

| Method | Equivalent Weight of Regeneration System, kg |
|---|---|
| Vapor diffusion | 744 |
| Vapor diffusion with compression | 782 |
| Multifiltration (sorption)* | 168 |

*Suitable only for regeneration from a condensate of atmospheric moisture.

It follows from the data that the equivalent weights vary from 710 to 833 kg depending on the method of regeneration. We have not listed any values here for the equivalent weights of systems based on methods of electrodialysis and reverse osmosis, inasmuch as they do not provide a high degree of extraction of water from vital activity products. /128

In developing systems for water supply, particular emphasis is placed on the organization of the processing of the wastes: jointly, separately or in combination.

We can think of five basic versions:

1. Urine, condensate of atmospheric moisture, and water used for sanitary and hygienic purposes processed separately.

2. Urine processed separately, with the condensate of atmospheric moisture and the water used for sanitary-hygienic purposes being processed jointly.

3. Urine and sanitary-hygienic water processed together, with the condensate of atmospheric moisture processed separately.

4. Urine and the condensate of atmospheric moisture processed jointly, with water used for sanitary and hygienic purposes processed separately.

5. All of the moisture-containing wastes processed jointly. On the basis of the "equivalent weight of the regeneration system productivity" ratio, it is most advantageous to process all of the waste products together. This simplifies the design and control of the system. However, this is advantageous only for the conditions that exist during prolonged space flights, assuming processing of large amounts of waste. For a comparatively high productivity, it will obviously be better to use separate processing. In fact, in a 366-day experiment (Burnazyan et al., 1969) the condensate of atmospheric moisture was processed by the sorption method, which involves the least energy consumption; the urine was processed by the oxidation-catalytic method and the water used for sanitary-hygienic purposes was processed by the coagulation method.

In a 90-day experiment (Jackson, 1970) urine and the condensate of atmospheric moisture were processed by the method of evaporation in a stream of air and vacuum distillation with catalytic oxidation; the water used for sanitary and hygienic purposes was processed by the multifiltration method (sorption).

For space stations with a six-man crew, a lifetime of 2 years and partial replacement of equipment after 6 months, the following combination of methods is suggested (Brose, Jackson, 1971):

- polluted water from bathing, showering and washing underwear and dishes should be processed by the method of reverse osmosis;
- the condensate of atmospheric moisture should be purified by multi-fraction (sorption);
- urine and the concentrate which remains following regeneration of water by the reverse osmosis method should be purified by evaporation involving vapor compression.

At the present time, it is difficult to make a final choice of a system for use on space flights in view of the various degrees of development of water regeneration methods.

## Water Supply Systems of the Apollo Spacecraft and Ground Experimental Facilities

### Water Supply System of the Apollo Spacecraft

The water supply system of the Apollo spacecraft is based on the use of water produced as the result of operation of fuel cells for drinking and preparation of food and the use of the condensate of atmospheric moisture for the thermoregulation system (Sauer, Shea, 1969, 1971). /129

There are systems in both the command and lunar modules. They provide the following: 1) supply and storage of water, 2) transportation of water to the locations where it is used for drinking and preparation of food, 3) use of water for cooling the cabin, 4) conducting the condensate of atmospheric moisture into a container for storage of water for technical purposes or for cooling the craft.

The principal difference between the water supply systems in the command and lunar modules is the fact that the water supply in the command module is based on the utilization of water which is obtained as a byproduct of the fuel cells (in the power supply system of the craft). There are no fuel cells in the lunar module. Therefore the water supply system is based on reserves. In addition, provision is made in the command module for heating and cooling water, but not in the lunar module. Some of the water in the lunar module is used for cooling the cabin by evaporation in a high vacuum.

The diagram of the water supply system for the crew in the command module is shown in Figure 39, while Figure 40 shows the system used in the lunar module.

The fuel cells are located in the service module and the water enters the command module through a pipe. As it passes through the distribution panel, the drinking water enters a storage container and then enters the food preparation unit. If the drinking water container is full, the water runs into

the container for water used for technical purposes. The condensate of atmospheric moisture enters either the container for water for technical purposes or is dumped overboard.

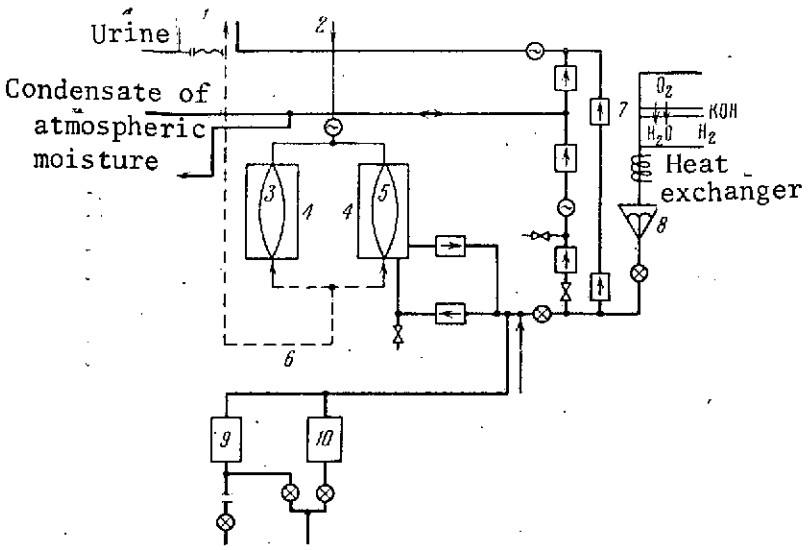



Figure 39. Water Supply System of the Command Module of the "Apollo" Spacecraft (According to Data of Sauer et al., 1960) 1, Regulating valve to space; 2, Oxygen hose; 3, Flexible container for urine; 4, Metal containers; 5, Flexible container for collecting drinking water; 6, Hose for urine; 7, Fuel cell (approximately 150°, 4.2 atm); 8, Water reservoir (24°, 4.2 atm); 9, Cooler (0.2 liter, 7°, 1.7 atm); 10, Heater for preparing food (1 liter, approximately 70°, 1.7 atm).

The fuel cells are composed of two chambers separated by porous nickel electrodes and containing concentrated potassium hydroxide as an electrolyte. One chamber is filled with oxygen (cathode) and the other is filled with hydrogen (anode). The pressure in the two chambers is 4.2 atm. The oxygen diffuses through the electrode into the hydrogen-filled chamber, where water is formed as the result of the interaction of the two elements. The electromotive force which is produced is used as the energy supply of the command module. The fuel cells operate at t = 150° and 4.2 atm and provide water at a nominal rate of 0.5 liters/hour. Productivity is a function of the power drawn from the fuel cells and can increase up to 0.9 liter/hr. Before the water from the fuel cells enters the command /131 module, the water is cooled to 24° and the pressure simultaneously decreases to 1.7 atm.

A typical chemical analysis of the water which is obtained from fuel cells is shown in Table 27. The chemical composition of the water from the fuel cells corresponds to that of distilled water, but it is saturated with hydrogen.

Water Supply System of the Command Module

The water from the fuel cells enters a separator at 24° and P = 1.7 atm to /132 remove the hydrogen, then goes to a distribution panel. The separator consists of a palladium-silver tube through which the hydrogen diffuses from the water into the vacuum of outer space (Figure 41). The principal elements of the distribution panel are: 1) two cutoff valves, one for the drinking water system

and the other for water used for technical purposes, 2) a cutoff valve which permits access to the system used for technical water, 3) chlorine supply system, 4) valve for admitting water to the vacuum of outer space, 5) two pressure regulators. This system makes it possible to connect the fuel cells with the drinking water container or the container for the water used for technical purposes and to dump the excess drinking water overboard. Using a bypass line, some of the water from the container can be used for cooling, heating or filling the container with water for technical purposes, or may be dumped overboard. A pressure of 1.7 atm is maintained by the oxygen which is necessary for inflating the polyisoprene chamber in the drinking water container. If the container of drinking water is full, the water from the fuel cells and the condensate from the atmospheric moisture (command module and space suit) enters the container used for water for technical purposes and may be dumped overboard or may go to two evaporators that act as secondary heat exchangers for the cooling system in the command module.

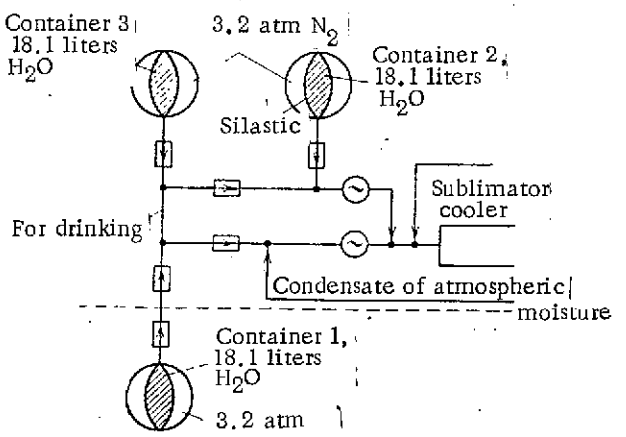



Figure 40. Water Supply System for the Crew of the Lunar Module of the "Apollo" Spacecraft.

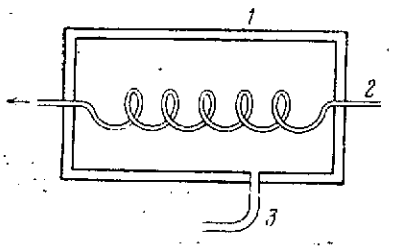



Figure 41. Diagram of the Elimination of Hydrogen from the Water from the Fuel Cells. 1, Diffusion chamber; 2, Silver-palladium tube for carrying water saturated with hydrogen; 3, Tube for dumping hydrogen overboard.

The following are the characteristics of the individual elements of the water supply system in the command module.

The drinking water container is used as a reservoir to store 18 liters of water in case the fuel elements break down and as a container for meeting sudden increases in the demand for water. The vessel has a cylindrical shape and is made of aluminum alloy. Inside the container is a chamber made of polyisoprene, filled with oxygen at a pressure of 1.7 atm. The oxygen is supplied by the general oxygen supply system.

The container of water used for technical purposes is used to store water for supplying the evaporator in the event that the main cooling system breaks down. The container holds 25 liters of water and is similar in design to the drinking water container.

TABLE 27. CHEMICAL COMPOSITION AND PHYSICAL CHARACTERISTICS OF FUEL CELL WATER

| Parameters | Fuel Cell | | |
|---|---|---|---|
| | A | B | C |
| pH | 7.0-7.5 | 7.0-7.5 | 7.0-7.5 |
| Specific electrical conductivity, $\mu mho \cdot cm^{-1}$ (approximately 24°) | 0.59 | 0.59 | 0.59 |
| Total amount of dissolved solids, mg/liter | 0.69 | 0.75 | 0.76 |
| Total amount of suspended matter, mg/liter | < 0.1 | < 0.1 | 0.2 |
| Total amount of solids, mg/liter | < 0.79 | 0.85 | 0.96 |
| Total amount of organic substances, mg/liter | 0.07 | 0.06 | 0.05 |
| Nonvolatile substances, mg/liter | < 0.62 | < 0.79 | None |
| Taste and smell, points | None | None | None |
| Cloudiness (Jackson units) | 0.8 | 0.8 | 0.7 |
| Chromaticity, degrees | 1 | 1 | 1 |
| Ionic composition, mg/liter | | | |
| Cadmium | < 0.01 | < 0.01 | < 0.01 |
| Chromium | < 0.01 | < 0.01 | < 0.2 |
| Copper | 0.20 | 0.23 | 0.21 |
| Iron | 0.04 | 0.05 | 0.05 |
| Lead | < 0.1 | < 0.01 | < 0.01 |
| Manganese | < 0.05 | < 0.05 | < 0.05 |
| Mercury | < 0.005 | < 0.005 | < 0.005 |
| Nickel | 0.03 | 0.04 | 0.04 |
| Silver | < 0.01 | < 0.01 | < 0.01 |
| Zinc | 0.15 | 0.18 | 0.26 |
| Calcium | 0.4 | 0.4 | 0.3 |
| Magnesium | < 0.1 | < 0.1 | < 0.1 |
| Sodium | 0.25 | 0.29 | 0.82 |
| Potassium | 0.1 | 0.1 | 0.1 |
| Selenium | < 0.01 | < 0.01 | < 0.01 |
| Aluminum | 0.9 | 1.1 | 0.8 |

The water cooler, which has a capacity of 0.2 liter, lowers the water temperature from 24 to 7° for drinking purposes. The material is stainless steel. The water is cooled by a water-glycol cooling system installed aboard the craft. /133

The food preparation unit consists of a heater and two measuring faucets. The heater contains about 1.1 liters of water and dispenses it at about 70°. It is made primarily of stainless steel.

The mouthpiece for drinking water is connected to the water supply system by a "Vitan" hose (177 cm).

The tubes are made of 6-mm aluminum tubing.

Preservatives: sodium hypochlorite (NaOCl).

Decontamination system. Five days prior to the launch, the water supply system in the command module is filled with deionized water containing 12 mg/liter of NaOCl. After four hours of exposure the water is drained and the system flushed with water which has been deionized by means of cellulose acetate membranes. After the system has been flushed it is refilled with ionized water. Three hours prior to launch, sodium hypochlorite is added to the system from a 20 ml ampoule containing 5,000 mg/liter of chlorine as well as $NaH_2PO_4$(0.7 M). During the flight, the drinking water supply system is subjected to the following decontamination operations:

a) if the drinking water container is full, the water can flow through the mouthpiece or the food preparation unit. This makes it possible for the water from the fuel cells to pass through the point at which the preservative is added and to enter the drinking water container;

b) NaOCl is added from a 20 ml ampoule with a chlorine concentration of 5,000 mg/liter and an aqueous solution of $NaH_2PO_4$(0.7 M);

c) during the 10 minutes of contact, the solutions that have been added mix with the water from the fuel cells in the section of tubing where the line from the technical water supply system branches off;

d) after 10 minutes contact, the ampoule of water is removed via the same opening through which it was added;

e) an additional 20 minutes period is provided before the water is used. These operations ensure total decontamination.

## Water Supply System Of The Lunar Module

The water supply system in the lunar module is based on reserves. The water is stored in three containers (Figure 41). The main container contains about 181 liters of deionized water; it is located in the part of the lunar module which is ultimately discarded, and provides the astronauts with water after they undock from the command module and land on the lunar surface, as well as during their stay on the Moon. When they take off from the lunar surface and dock with the command module, they use the water stored in the two containers with a capacity of 18.1 liters.

The lunar module water supply system is made of aluminum treated with alodine. The water is stored in containers made of Silastic. The space between the container and the container housing is filled with nitrogen at a pressure of 3.2 atm. The sublimation assembly consists of the heat exchangers and is intended for the cooling system. It consists primarily of nickel sheets /134

which form a boundary between the water-ice phases on the one hand and the vacuum of space on the other. Iodine was chosen as the preservative because chlorine impedes the sublimation process. Seven days prior to launch the water supply system of the lunar module is filled with an iodine solution having a concentration of 30 mg/liter. After one hour the system is drained and refilled with deionized water containing 10 mg/liter of iodine. This is the water which is used during the flight.

The hydrophobic-hydrophilic gas-liquid separator functioned normally aboard the Apollo-11. After Apollo-12 the silver-palladium separator was always used (see Figure 41) (Ellis, Willes, 1967).

The operation of the water supply system reveals the following characteristic features. The preservatives that were used produced corrosion of the structural materials. Three points with maximum corrosion activity were found: the place where the tubing enters the heater, the place where the mouthpiece and the hose come together, and the part of the tubing between the point at which the chlorine is added and the container with drinking water. It was also noticed that iodine interacted with the Silastic membranes in the drinking water containers aboard the lunar module. An organic sediment was found in the water.

The astronauts noticed the change in the color of the drinking water during the flight. By means of infrared spectroscopy the organic compounds were identified as being part of the plasticizer in the vinyl polymers. The only source of these compounds was the flexible hose connecting the mouthpiece and the water supply system, made of neoprene material. Replacing the latter by a hose made of Viton allowed this problem to be solved.

Water Supply System of Ground Experimental Facilities

In 1966, 62-day tests of the life support system were carried out in a model of the spacecraft. The water supply system included units for regeneration of water from urine, the condensate of atmospheric moisture and water used for sanitary-hygienic purposes (Secord, Bonura, 1966).

The water from urine and the condensate of atmospheric moisture were regenerated by a combination of methods: filtration, evaporation in a stream of air, and electrodialysis (Figure 42). Extraction of water from used sanitary-hygienic water supplies was accomplished by filtering through a series of mechanical filters and sorption columns. Regardless of the positive results obtained in this experiment, the electrodialysis method was later /136
dropped from the water supply system; in subsequent 60-day tests the method of evaporation in a stream of air and multifiltration were used.

60-day tests of life support systems in a spacecraft cabin simulator with a 4-man crew were conducted in the USA on 19 April 1968 by the firm of McDonnell-Douglas.

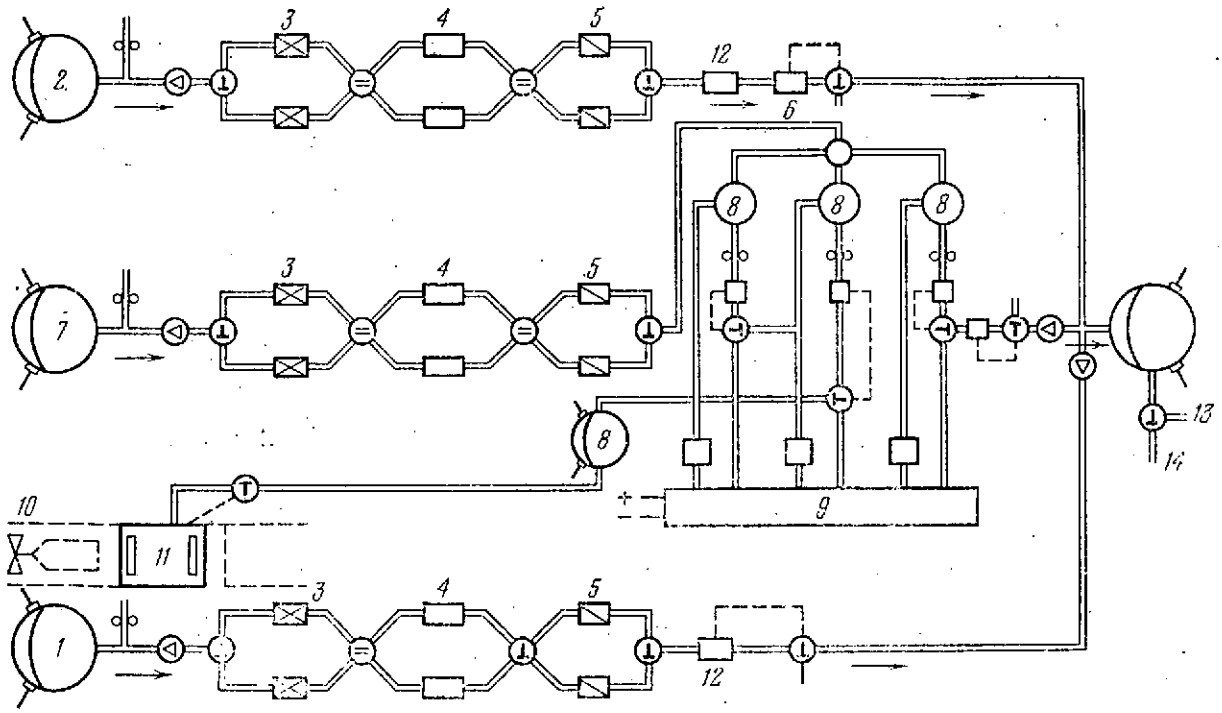



Figure 42. Diagram of the Water Supply System Tested in the 62-Day Experiment (According to Secord and Bonura, 1966).
1, Receiving container for collecting condensate; 2, Container for water used for sanitary and hygienic purposes; 3, Ion-exchange filters; 4, Activated charcoal filters; 5, Bacterial filters; 6, Ultraviolet cell of colorimeter; 7, Urine container; 8, Intermediate containers; 9, Electrodialyzer; 10, Fan to blow air from cabin; 11, Evaporator; 12, System for checking water quality; 13, Hose for drinking water; 14, Water pipe for repeated regeneration.

The water supply system consisted of a unit for the regeneration of drinking water from urine and the condensate of atmospheric moisture and a unit for the purification of water used for sanitary and hygienic purposes. The regeneration unit for drinking water was based on the method of evaporation of water from urine and atmospheric moisture and included the following main units (Figure 43): urine collector, preliminary processing unit, evaporator, condenser-separator, silver ion generator, filter, decontamination unit, four containers of hot water and a device for ensuring supplies of hot and cold water. /137

The purification of water used for sanitary and hygienic purposes was based on the processes of multifiltration and included bacterial filters, columns with activated charcoal and ion-exchange resins, a container for

storing water and a device to supply hot and cold water (Figure 44). The unit for regeneration of drinking water was initially designed for reprocessing urine, the condensate of atmospheric moisture, the condensate for the thermoregulation system and the condensate that was obtained in the regeneration of silica gel cartridges used in the $CO_2$ elimination system. Initially, water was regenerated from all of these sources. However, it was subsequently decided that two crew members would use regenerated water and two would use distilled water. Hence, reprocessing of condensates from silica gel cartridges and from the thermoregulation system was suspended on the 10th and 36th days, respectively.

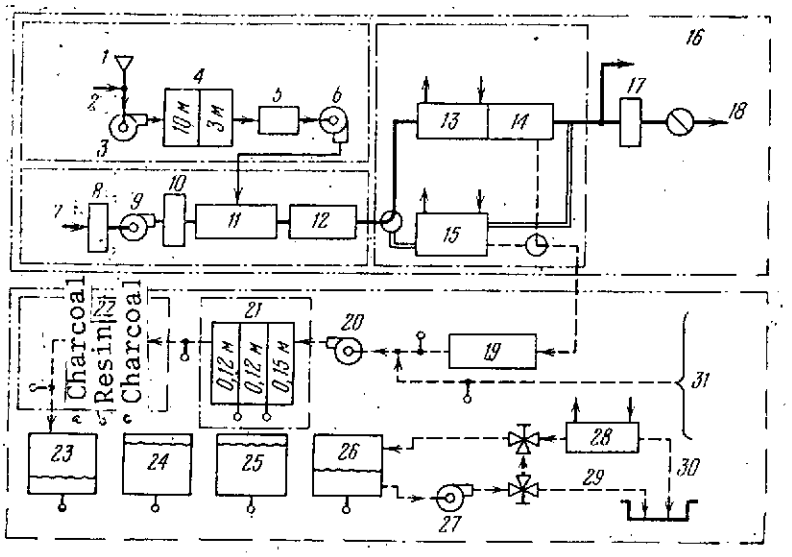



Figure 43. Diagram of the Drinking Water Regeneration System in the 60-Day Experiment.
1, Chamber for preliminary chemical processing; 2, Hose to supply urine and wash water; 3, 6, 20, 27, Pumps; 4, 8, 17, Filters; 5, Containers; 7, Cabin atmosphere; 9, Gas blower; 10, Heater; 11, Evaporator; 12, Activated charcoal; 13, 15, Condensers; 14, Separator; 16, To $CO_2$ concentrator; 18, Hose to feed air to cabin; 19, Silver ion generator; 21, 22, Filter blocks; 23, Container of hot water; 24, Water analyzer; 25, Container for water supply; 26, Container for used water; 28, Cooler; 29, Water pipe for hot water; 30, Water pipe for cold water; 31, Condensate of atmospheric moisture collector.

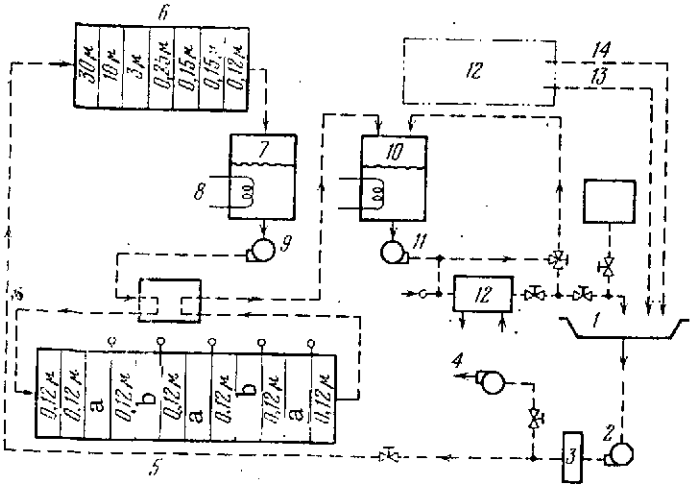



Figure 44. System for Regeneration of Water Used for Sanitary and Hygienic Purposes in the 60-Day Experiment.
1, Pan with a 100-mesh grating; 2, 9, 11, Pumps; 3, Filter; 4, Line for dumping water overboard; 5, 6, Filter blocks; 7, Water container; 8, Heater for sterilization; 10, Hot water container; 12, Cooler; a, Charcoal; b, Resin.

The following are the characteristics of the individual elements of the system used on the 60-day experiment. The air-evaporation unit was intended for collection, preliminary chemical processing and supply of urine to the evaporator where the water was evaporated in a stream of air coming from the cabin, then returned to the latter, as well as for condensation of water vapor separated from /138 urine and from the cabin atmosphere. The urine collector consists of the urine-receptacle funnel, a fluid dispenser for preliminary processing, a pump for transferring the urine, containers with a solution for washing out the urine receptacle, valves and hoses. The fluid for preliminary processing (preservative) consists of sulfuric acid, chromium trioxide and copper sulfate. Four ml of solution are required for each liter of urine. The rinse water was needed to eliminate the odor from the urine receptacle. When the valve was opened in the urine receptacle the mixture of urine, rinse water and preservative was transported by means of a pump through 10 and 3-micron filters into the receiver. At a volume of one liter, a signal from an electronic level senser triggered the transfer of the mixture to the evaporator. The components of the evaporator are an air filter, gas blower, heater, six evaporation chambers, a charcoal filter to purify the air and a control system. The gas blower pumps the air from the cabin through 1-micron filters into the electrical heater where the temperature is raised to 43°. The hot air evaporates the urine in one of the chambers and passes into the condenser-distributor, where condensation of water vapor takes place at reduced temperature and the fluid droplets are separated from the air which is being transported. The dried air returns to the cabin, passing through a 1-micron filter. Two types of condensers were used. One was the usual kind of condenser used for terrestrial conditions, which functioned in case of breakdown or during testing, while the other was a condenser-distributor intended for weightless conditions. The latter is composed of a condensing heat exchanger, separator and water supply device. The separator guides the droplets of water out of the stream of air

onto a conical hydrophobic membrane. The water droplets move across the conical membrane, collect and fall onto hydrophilic porous metal plates which draw off the water and do not allow air to pass through them. The water is exhausted by a pump which supplies the water to the unit for additional purification. The latter consists of a bank of filters, a decontamination bank, containers of hot water and a distributing device. The filter bank uses bacterial filters with a pore size of 0.12-0.15 microns as well as two columns with activated charcoal and one column with ion-exchange resins. After passing through the unit for additional purification the water enters the containers where a temperature of about 70° is constantly maintained to prevent the growth of microflora. The volume of the container is 35 liters.

The water supply system uses an ionator which is intended for generating silver ions for the purpose of decontaminating the water obtained from urine. The dimensions of the ionator are as follows: diameter 6 cm, length 10 cm; weight 300 grams. The electrical circuit of the ionator is shown in Figure 45. The ionator consists of a silver anode with a high degree of purity, an aluminum-silver cathode, an aluminum electrode and teflon coatings; its electrical power supply consists of three 1.5 volt silver oxide batteries designed for 9,000 hours service. The ionator can work either in a stream of water or under static conditions. The average power required for the water regeneration system is 1.127 kW. The power distribution by units is as follows: gas blower 0.194 kW, air heater 0.431 kW, drinking water heater for containers 0.502 kW. These values do not include the energy consumption required for the operation of the pumps. /139

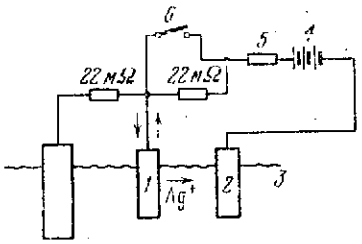



Figure 45. Diagram of Generator to Obtain Silver in Ionic Form in a 60-Day Experiment.
1, Anode; 2, Cathode; 3, Water (electrolyte); 4, Power source; 5, Resistor; 6, Switch.

The unit for generation of drinking water supplied the crew with water for the whole experiment, except after the 39th day. At this time growth of microorganisms in the drinking water container was detected. The quality of the regenerated water is shown in Table 28.

It follows from the table that the regenerated water satisfied normal standards. A characteristic feature of the water used by the volunteers was its negligible mineralization. Practically speaking, the crew used distilled water which had not gone through the stage of enrichment with salts and trace elements. /140

The main balance characteristics of the water regeneration unit for obtaining water from urine and the condensate of atmospheric moisture are shown in Table 29 and in the diagram.

TABLE 28. QUALITY OF DRINKING WATER REGENERATED FROM URINE AND THE CONDENSATE OF ATMOSPHERIC MOISTURE IN A 60-DAY EXPERIMENT

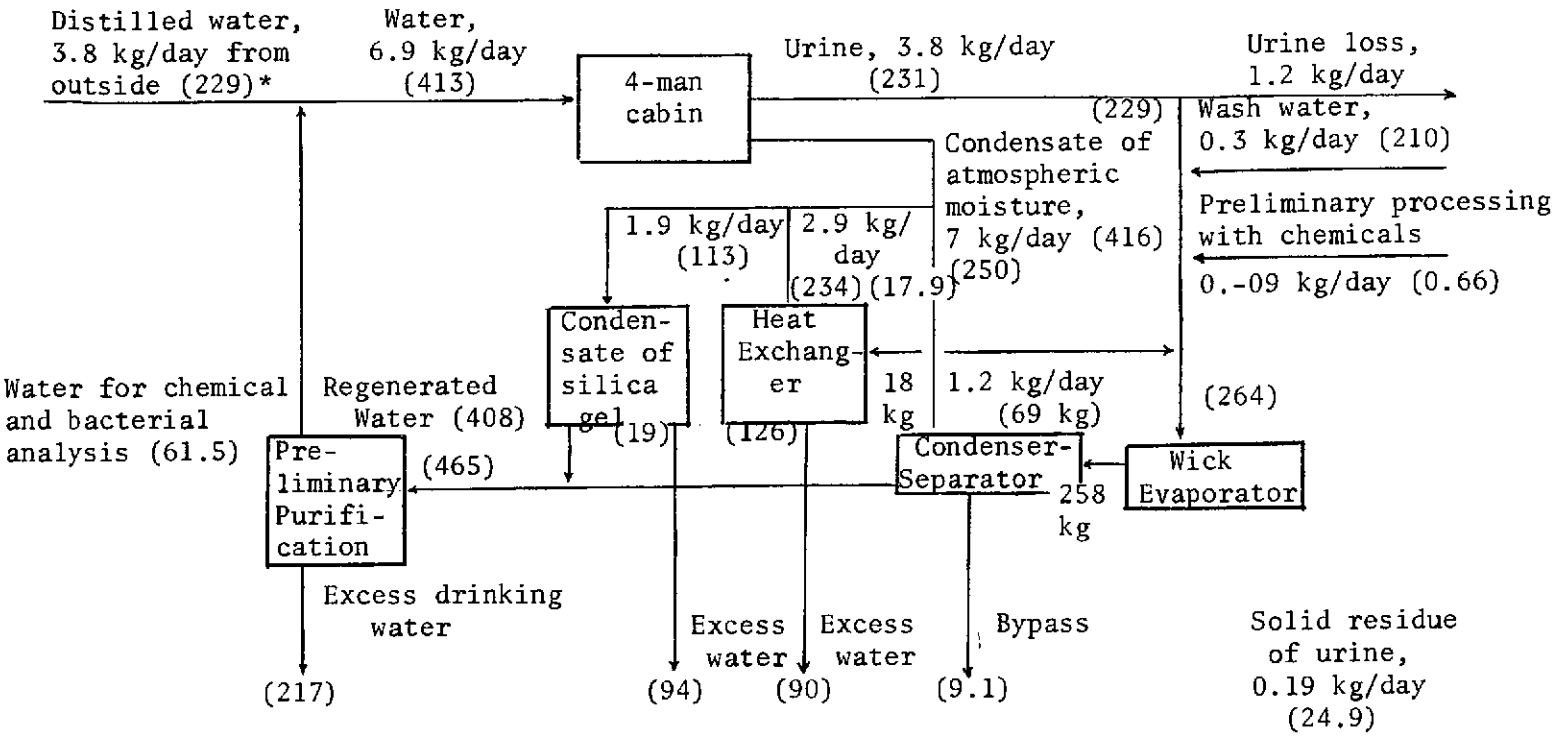
| Parameters | Water | | Standard |
|---|---|---|---|
| | Before the Fine Purification Assembly | From the Container | |
| Cloudiness, in Jackson units | -- | 2.1-5 | 10 |
| Chromaticity, Co-Pt scale units | -- | 3.8-5 | 15 |
| pH | 8.3 | 6.3-8.7 | -- |
| Specific electrical conductivity, $\mu mho \cdot cm^{-1}$ | 770 | 36-420 | -- |
| Ammonia, mg/liter | 110 | 4.8-12.5 | -- |
| Bichromate oxidability, $O_2$ mg/liter | 269 | 77.1-166 | 100.0 |
| Ethanol, mg/liter | 118 | -- | -- |
| Aldehydes, mg/liter | 1.7 | -- | -- |
| Aluminum, mg/liter | 0.02 | 0.28-0.46 | -- |
| Calcium, mg/liter | 0.11 | 1.97-4.64 | -- |
| Silver, mg/liter | 0 | 0.01-0.02 | 0.5 |
| Chlorides, mg/liter | 0 | -- | 450.0 |
| Sulfates, mg/liter | 0 | 0 | 250.0 |

TABLE 29. BASIC BALANCE CHARACTERISTICS (in liters/day) FOR THE REGENERATION UNIT FOR DRINKING WATER (per man)

| Components | Planned Values | Actual Values | |
|---|---|---|---|
| | | Per Day | Total amount, liters |
| Urine | 1.78 | 0.96 | 231 |
| Solid urine residue | 0.08 | 0.047 | 11.28 |
| Wicks | -- | 0.0188 | 4.53 |
| Condensate of atmospheric moisture | 1.372 | 1.730 | 416.579 |
| Total amount of water obtained | 3.085 | 2.650 | 635.831 |
| Water for analyses | -- | 0.258 | 62.016 |
| | | 0.802 | 192.525 |
| Excess water | -- | 0.906 | 217.44 |
| Added from outside | -- | 0.954 | 228.765 |
| Total consumption of water | 2.867 | 1.724 | 413.589 |

These data indicate a slight difference between the proposed and actual values of the balance characteristics. The decrease in the quantity of urine and the increase in the condensate of atmospheric moisture was due to the warm dry atmosphere in the spacecraft cabin simulator which increased perspiration and decreased diuresis.

DIAGRAM OF BALANCE CHARACTERISTICS OF THE WATER REGENERATION UNIT FOR OBTAINING WATER FROM URINE AND THE CONDENSATE OF ATMOSPHERIC MOISTURE IN A 60-DAY EXPERIMENT




*The value (in kg) of the total amount of product for tests is given in parentheses.

In September 1970, a 90-day experiment involving participation of four subjects was completed in the USA. The principal purposes were:

- checking the effectiveness of functioning of the life support system for the crew, particularly the water supply system;
- determination of the characteristics and the energy consumption of the life support systems;
- studying the ability of the crew members to control the equipment in the cabin;
- study of the chemical and microbial composition of the environment and many others.

The water supply system was based on regeneration processes and included a subsystem for regeneration of water from urine, the condensate of atmospheric moisture and water used for sanitary-hygienic purposes (Putnam, Thomas, Colombo, 1970).

The system for regeneration of water from urine and the condensate of atmospheric moisture was based on two methods: 1) evaporation in a current of air with subsequent purification by ion-exchange resins and activated charcoal and 2) vacuum distillation with catalytic oxidation. /143

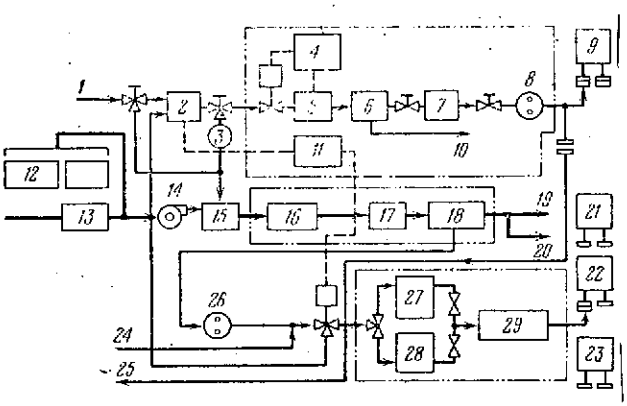


Figure 46. Diagram of Drinking Water Regeneration System in a 90-Day Experiment. 1, Hose from urine receptacle; 2, Urine collector; 3,8,26, Pumps; 4,11, Level sensors; 5, Boiler; 6, Condenser; 7, Intermediate container; 9, Water container; 10 10, Tube into space; 12, Coolant; 13, Drier for underwear; 14, Gas blower; 15, Wick evaporator; 16, Activated charcoal; 17, Filter; 18, Condenser-separator; 19, Pipe for returning air to cabin; 20, Tube to $CO_2$ concentrator; 21,22, 23, Containers for water; 24, Pipe to supply atmospheric moisture condensate; 25, Water pipe leading to atmospheric regeneration system; 27,28, Containers for hot water; 29, Multifiltration module.

The water used for sanitary and hygienic purposes was processed by the multifiltration method. Diagrams of the regeneration systems for drinking water are shown in Figures 46 and 47. Urine which had previously been treated with preservative was fed into the boiler. The preservative was composed of 39.8% $H_2SO_4$, 47.3% $H_2O$, 9.8% $CrO_3$ and 3.1% $CuSO_4$. Four ml of preservative were required to treat one liter of urine; it had a specific gravity of 1.42 g/ml. The source of heat energy was composed of four capsules containing a radioisotope of plutonium-238 ($PuO_2^{238}$) (see Figure 48) (Metzger, 1970). The power of each capsule was 75 W. The temperature of the distillation process was 37° and the pressure was 48 mm Hg. The vapor that was formed and

the volatile components were heated to 115-138° by means of a capsule containing $PuO_2^{238}$, with a power of 45 W. After passing through the oxidation stage, the vapor phase entered the condenser and was then turned into water without additional purification; this water then went into the collector. In those cases when the regenerated water did not satisfy standards in terms of odor, taste or microbiological contamination, it was sent to the sorption purification unit and decontaminated. In contrast to previously described catalysts, working at a temperature of about 650°, in this experiment a low-temperature catalyst known as Ardox was used which makes it possible to decrease the temperature of the catalytic oxidation to 138°.

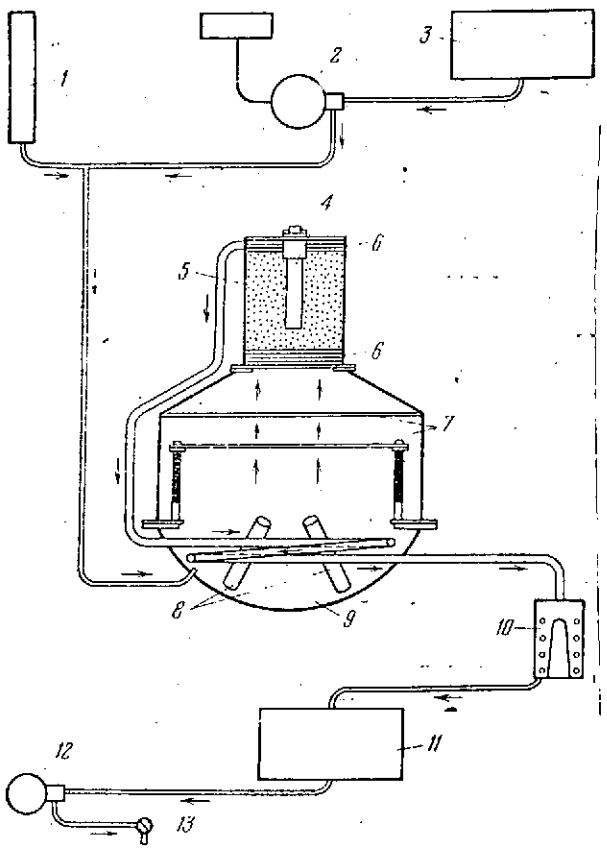



Figure 47. System for Regeneration of Water with Radioisotope Energy Source.
1, Manometer; 2, Pump; 3, Urine collector; 4, Capsule containing radioisotope (45 W); 5, Catalyst; 6, Glass wool; 7, Membrane; 8, Capsule containing radioisotope (75 W); 9, Evaporator; 10, Condenser; 11, Drinking water receiver; 12, Pump; 13, Hose for user of drinking water.

The amount of water which is supplied from the cabin to the water regeneration system from urine and is necessary for the oxidation of organic compounds was 12-14 $cm^3$/minute. The dimensions of the capsules containing $PuO_2^{238}$ were as follows: diameter 2.54 cm, length 11 cm, wall thickness 0.076 cm. The structural material of the capsule was tantalum with 10% tungsten. The calculated time of operation of the radioactive source for the heat energy was 5 years.

The water regeneration system based on vacuum distillation with catalytic oxidation functioned for a total of 63 days (after 25 days the boiler was replaced). During this period of time, more than 666 liters of urine and condensate of atmospheric moisture were purified with a degree of extraction of 94.3%. Of this amount, 360 liters of water required additional purification by means of ion-exchange resins and activated charcoal.

During all of this time, spattering of urine into the catalytic reactor was observed, making it necessary to wash the catalyst. As a backup, the researchers used a water regeneration system based on evaporation in a stream of air (Figure 46). The urine, after first being treated with a preservative, was fed into a wick evaporator 15 where the hot cabin air eliminated water vapor from the urine and the volatile compounds were eliminated as well; they then passed through a cartridge 16 filled with activated charcoal. The water formed in condenser-separator 18 passed on to containers 27, 28 where sterilization at 71° was carried out for 6 hours. Then the water treated in this fashion went to sorption purification unit 29 and then to containers 21-23. /144

In the regeneration of water from a condensate of atmospheric moisture, the latter does not enter evaporator 15. In this case the air from the cabin travels through the bypass line directly into condenser-separator 18 which can function under weightless conditions. The latter is accomplished by using hydrophobic-hydrophilic membranes. Hydrophilic membranes are made of stainless steel; hydrophobic ones are made of stainless steel covered with teflon. The water is removed by a vacuum cylinder and a pump.

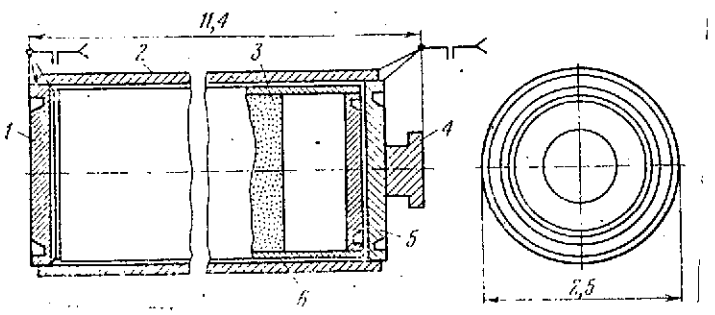



Figure 48. Capsule With Isotope Heat Source Using $Pu^{238}O_2$.

1, Lid; 2, Pipe; 3, $Pu^{238}O_2$; 4, Lid with cap; 5, Insert; 6, Liner.

This system functioned for 31 days and processed 317 liters of urine and wash water with 100% extraction. The condenser-separatory 18 processed 1,438 liters of water (from the wick evaporator and the cabin atmosphere). It was observed that on the 83rd day the vacuum cylinder in the water elimination unit had to be replaced because a spring broke. The unit for additional purification of water obtained by the method of vacuum distillation with catalytic oxidation consisted of one filter, a column with activated charcoal. The weight of the sorption layer in each column was about 100 grams. During the additional purification of water obtained by the method of wick evaporation 0.54 kg of activated charcoal and 0.54 kg of ion-exchange resin was used. During the experiments, the sorption layer was changed three times because of increases in ammonia concentration or total amount of organic substances. In all, the additional sorption purification unit processed more than 800 liters of water obtained from urine and the condensate of atmospheric moisture.

The system for regeneration of water used for sanitary-hygienic purposes (Figure 49) is based on the multifiltration system and is intended for /145

purification of contaminated water resulting from hygienic procedures (washing, showering, etc.) as well as the laundering of underwear and wiping up in the cabin. The basic elements of this system are the following: a bank of filters 5-11, heat exchanger 17, mixer, pump 14 (washing machine and drier). The washing compound was a concentrated organic biodegradable substance known as Basic H, without additives. The filter assembly consisted of a series of filters with pore diameters of 30, 3 and 1 micron as well as columns containing activated charcoal, two columns with ion-exchange resin and one column containing activated charcoal.

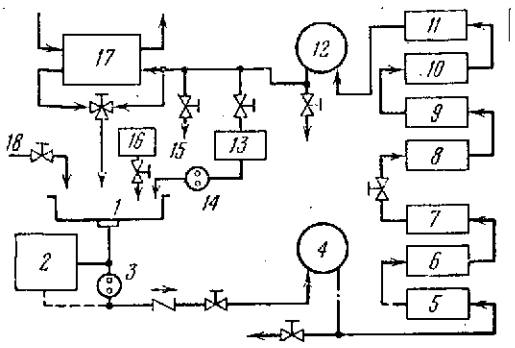



Figure 49. Diagram of a System for Regeneration of Sanitary-Hygienic Water Based on Multifiltration. 1, Receiver-screen; 2, Level sensor; 3,14, Pumps; 4,12, Containers of hot water; 5, Filter (30 microns); 6, Filter (3 microns); 7, Filter (1 micron); 8,11, Activated charcoal; 9,10, Ion-exchange resins; 13, Container for water after laundering and washing; 15, Hose for rinsing out urine receptacle; 16, Container for washing compounds; 17, Heat exchanger; 18, Hose from drinking water system.

Water used for sanitary and hygienic purposes entered the container with hot water, automatically passing through a series of filters and entering a second container with hot water 12. The temperature of the water entering for use was regulated manually, with heat exchanger 17 provided for the purpose. The total amount of water processed for sanitary and hygienic purposes was 5,000 liters. During the entire experiment, one column of activated charcoal was replaced (4 times), as were two columns with ion-exchange resins (once) and five mechanical filters. The need for filter replacement was indicated by a rise in the pressure in the system caused by blockage of the filters by mechanical particles. Replacement of sorption columns was carried out in accordance with the evaluation of the subjects as well as on the basis of results from chemical and bacteriological analyses. The total weight of the sorbents used was about 11 kg. The washing machine and drier were used to wash and dry underclothing, socks, uniforms, towels and sheets. In addition to the water regeneration banks in the water supply system, there were also supplies of drinking water. The drinking water, 181 liters of it, was stored in stainless steel containers. The preservative was iodine at a concentration of 5 mg/liter. However, this water was not used during the /146
experiments since the water needs were met completely by the regenerated water. The chemical composition of the water obtained from urine, condensate of atmospheric moisture and used sanitary-hygienic water was as follows:

| | Drinking Water | Water Used For Sanitary-Hygienic Purposes |
|---|---|---|
| Organic carbon, mg/liter | 3-33 | 81-429 |
| Ammonia, mg/liter | 0-19 | -- |
| pH | 4.2-7.0 | 3.0-7.6 |
| Chromaticity, points | 0-8 | 0-4 |
| Odor | From very weak to weak | Weak |
| Bacterial contamination, microbes/ml | 0 | 0-6 |

According to most of the indicators the regenerated water satisfied the generally accepted standards. However, one can see that there were increased amounts of organic carbon (up to 429 mg/liter) in the regenerated water used for sanitary and hygienic purposes. This obviously was due to fats, which are not eliminated very effectively by ion-exchange resins and activated charcoal. In addition, both the drinking water and that used for sanitary and hygienic purposes are characterized by low pH values (4.2-7.0 and 3.0-7.6, respectively).

The energy consumption levels for the water regeneration system in the 90-day experiment are shown in Table 30.

TABLE 30. ELECTRICAL CONSUMPTION OF THE WATER REGENERATION SYSTEMS OF DIFFERENT KINDS

| Type of Regeneration System | Units of Regeneration System | Power, Watts |
|---|---|---|
| On the basis of vacuum distillation and catalytic oxidation* | Boiler | 268.5 |
| | Catalytic reactor | 73.5 |
| | Condenser | 362 |
| | Pumps | 9 |
| On the basis of evaporation in a stream of air | Weak evaporator | 101 |
| | Condenser | 105 |
| | Gas blower | 307 |
| | Pumps | 0.7 |
| Additional purification | Container-sterilizer | 163 |
| On the basis of the multi-filtration method | Container-sterilizer | 239 |

*Heat energy from an isotope source ($Pu^{238}$ $O_2$).

A considerable portion of the energy consumption by the system is due to the maintenance of a high temperature in the sterilizing containers. Use of effective chemical preservatives would have allowed reduction of total energy consumption. /147

A ground complex of life support systems has been developed in the Soviet Union, and in accordance with the program for the conquest of space a one-year medical-technical experiment was performed between 5 November 1967 and 5 November 1968. The crew was composed of three men: a physician, G. A. Manovtsev; a biologist, A. N. Bozhko, and a technician, B. N. Ulybyshev. The principal tasks involved in the experiment were the following (Burnazyan et al., 1969):

- to determine the feasibility of prolonged stay by man in a pressurized chamber with limited volume under conditions of utilization of decontaminated products of nutrition and utilization of oxygen and water regenerated from the waste products of human vital activity;

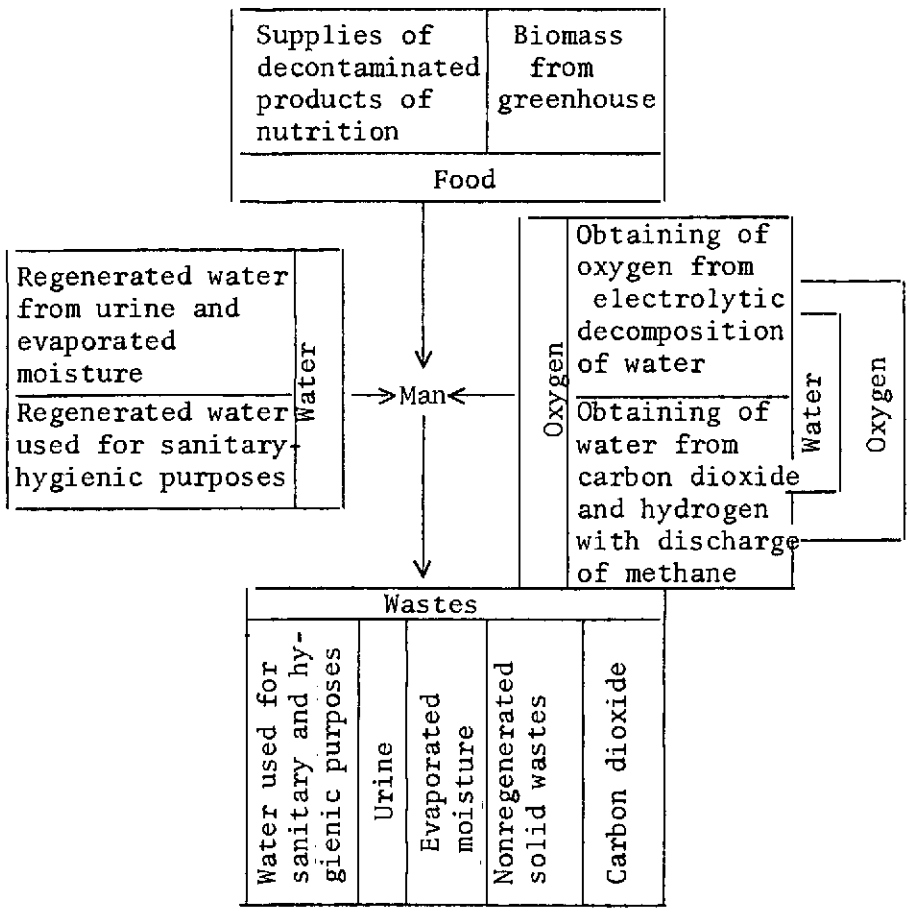
- the study of the changes in the environmental media as well as an investigation of the influence of conditions created by systems on the human organism;

- development of technological systems for the purpose of rational planning of systems for regeneration of oxygen, purification of the atmosphere and obtaining water from waste products of human vital activity.

The system included systems for water regeneration, purification of the atmosphere and regeneration of oxygen, as well as auxiliary devices. Mass-exchange in the ground complex of life support systems was on the block system. In addition, the system had a greenhouse to supply vitamins at one stage of the experiment. The water supply system was based on physico-chemical processes of regeneration. As drinking water sources, a condensate obtained by condensation of moisture from the spacecraft cabin or the greenhouse was used, as well as urine excreted by the crew.

The main process of water regeneration from urine was the oxidation-catalytic method, assuming the use of such stages as the preservation of urine, filtration, evaporation, oxidation of organic compounds to simple oxides on the surface of a heterogeneous catalyst, condensation of vapor, and additional sorption purification. Since the fluid thus obtained was similar to distilled water in chemical composition, in order to confer desirable qualities on it a stage of enrichment with salts and trace elements was to be provided. Since the daily consumption of drinking water was 2,500 ml per crew member and the amount of water in the daily portion of urine was 1,600 ml, the shortfall was made up by drinking water regenerated from the condensate of atmospheric moisture. For this purpose, a sorption-photochemical method was used which had the following stages: filtration, oxidation of organic compounds during irradiation of water by ultraviolet radiation, additional sorption purification, enrichment of water with mineral salts and trace elements. Regeneration of the water from used sanitary-hygienic water was performed by the coagulation method. The water used for washing dishes was regenerated by /148

means of an oxidation-catalytic method similar to the one used for extracting water from urine.




Prior to the start of the experiment the drinking water unit was filled with preserved water, since the regeneration system would not be receiving any products of vital activity during the first few hours for purely physiological reasons.

The system for regeneration of water from urine and the condensate of atmospheric moisture was connected to the living quarters in the first stage. In the first and subsequent stages the system for regeneration of water from urine provided drinking water in an amount of approximately 5 liters/day. The productivity of the system for purification of the condensate of atmospheric moisture was about 3 liters/day. For the preparation of food and for drinking, /149 the subjects used 2.5 liters of water per day per man.

In the second stage of the medical-technical experiment, the laboratory system for regeneration of sanitary-hygienic water was connected. Based on the coagulation method, this system had an average daily output of 23 liters of water.

In a third stage, the laboratory system for regeneration of water from cooking water was used, with an output of 10 liters per day. By adding this system it made it possible to achieve practically total recycling of the water.

During the one-year medical-technical experiment the regeneration system yielded 6,000 liters of water, of which 3,100 liters were obtained as the result of recycling of water used for sanitary-hygienic purposes and 2,900 liters came from urine and the condensate of atmospheric moisture.

# CHAPTER IV: CONDITIONING REGENERATED WATER

## Methods of Enriching Regenerated Water

Naturally, in designing water supply systems for spacecraft, it is /150
necessary to take into account a number of medical and biological aspects of design in addition to solving problems of a technical nature associated with the development of water regeneration methods. Besides the problems of standardizing regenerated water, they include for example such problems as its conditioning as well as comprehensive sanitary and hygienic evaluation. The conditioning of water can be subdivided into many different measures which ensure that it is given acceptable organoleptic as well as physical and chemical properties, in accordance with the requirements of the All-Union State Standards, and the quality of the drinking water is retained all during the flight. In this connection, the problem of conditioning the water is twofold: enriching the recovered water with salts, and decontaminating it.

The problem of enriching regenerated water with mineral components is closely linked to the problem of its decontamination. When the first regeneration systems for water were constructed, methods were proposed for regeneration that involved consideration of removal of all impurities that came from moisture-containing wastes. In practice, distilled water is formed at the outlet of regeneration systems; it lacks both organic and inorganic impurities. At the current level of development of life-support systems this approach is obviously more correct, inasmuch as it is better to add insufficient mineral components to the water than to separate them selectively in the fluid phase during purification. It is therefore natural that in addition to the development of regeneration systems for water the problem of conditioning the water has developed as well. An analysis of the data in the literature indicates that at the present time considerable attention is being devoted to the problem of conditioning water which lacks mineral components under natural conditions.

The majority of hygienists both in the Soviet Union and abroad (Kalmykov, 1964; Krotov, 1959; Margaret, 1945) feel that water which is low in minerals is incomplete both hygienically and physiologically, and point out the need for artificially enriching it with mineral components. However, the use of methods of enrichment under natural conditions, with the exception of the fluoridation /151
of water ,has not found wide application. This problem has received practically no consideration in the design of water-supply systems for spacecraft. In this connection, we conducted extensive studies in the area of evaluating existing methods of enriching water (as well as developing new ones), taking into account the influence exerted on the human organism by spaceflight factors. In studying methods of enriching the regenerated water, we were naturally compelled to consider aspects of both a medical-biological and technological nature. The former include (for example) problems of the physical significance and standardization in water of individual mineral components, taking into account the influence of spaceflight factors on water-salt metabolism in man. In developing the elements for conditioning water, it was

also necessary to give thought to the possibility of developing a salt-enrichment unit with minimum weight, size and energy consumption.

An analysis of the data in the literature indicates that the absence of mineral compounds in water leads first of all to a deterioration of its organoleptic properties, and also has a negative effect on water usage as well as several other physiological functions of the organism (Kondror, 1963; Shelukhin, 1955). According to the data of these authors, for example, use of desalinated water causes a drop in the demand for water by the population and in some cases even causes a total failure to drink (Suckling, 1948). In addition, prolonged use of salt-free water leads to adjustment to its taste (Ceryapa, 1965). It has also been established that distilled water, in comparison with tap water, satisfies thirst to an insufficient degree and under certain conditions, for example high temperature, it can contribute to hyperhydration of the organism (Drachev, 1963). However, prolonged usage of salt-free water by man can lead to a disruption of physiological functions of the organism and a number of problems that are associated with a deficit in the intake of certain mineral components into the organism, including trace elements. Thus, the authors point to the considerable biochemical changes involving the composition of the blood and urine (as well as the increased brittleness of the bones) of polar explorers who used glacier water for drinking for a year (Deryapa, 1965). Similar data are presented by authors in conjunction with the study of the influence exerted on the organism by low-mineral water from certain curative springs (Dudchenko, 1957). There are also figures on increased incidence of illness involving the digestive organs in individuals who used glacier water for long periods of time (Smirnova, 1963). Knorre (1898) mentions morphological changes that occur in the gastro-intestinal tract under the influence of distilled water, associated with the leaching of salts from the mucous membranes.

The biological role of individual mineral components, including water, has been studied a great deal. We know for example that insufficient intake of calcium with water can lead to a slowing down of the physical development of the organism and a disruption of the formation of bones (Margaret, 1945); the /152
important role of the water factor in this respect is indicated by data that imply that up to 1/3 of the human need for calcium may be covered by water (Shelukhin, 1955). In experiments on animals that received distilled water, a considerable lag in weight increase and growth was observed (Meyrs, 1935). It has also been found that one of the reasons for serious endemic diseases of the bone and joint system is insufficient calcium content in the drinking water (Vinogradov, 1949; Kaneath Beeson, 1945). We know that prolonged usage of salt-free water can lead to an insufficient intake of macroelements and trace elements into the organism which are of important physiological significance (Gabovich, 1957; Voynar, 1960).

Researchers have established for example that water plays an important role in the etiology of diseases involving insufficient intake of fluorine into the human organism (Gabovich, 1957). Thus, in regions where glacier water is used, the incidence of caries frequently reaches 70-95% (Meshchenko, 1962).

Insufficient intake of iodine into the organism with water and food products can cause development of widespread diseases of endemic goiter (Voynar, 1960). The relatively low specific gravity of the water in the iodine balance of the water (approximately 5%) and the possibility of compensating for its insufficient intake with water in regions where goiter is endemic by using imported food products, including iodized salt, has led a number of authors to deny the significance of the role of water in the etiology of this disease (Pechenkina, 1964).

We know, however, that in the course of cooking all food products lose from 14-65% of their iodine, and when iodized salt is stored for 3 months all of the iodine (100%) is lost (Goncharova, 1958). A further study of this problem has revealed the close correlation that exists between the iodine content in drinking water and the occurrence of goiter (Florinskiy, 1965). This has served as the basis for the development of methods of enriching the water with iodine in regions where goiter is endemic (Yakovlev, 1964).

Hence, the experience gained thus far indicates that fresh water is inadequate from the hygienic and physiological standpoints, so that most hygienists, both in the Soviet Union and abroad, recognize the necessity of enriching it with mineral components (Kalmykov, 1948; Krotkov, 1959; Margaret, 1945).

It has been established that certain changes in the water-salt metabolism of cosmonauts occur under the influence of spaceflight factors, taking the form of dehydration of the organism; there is also an increased excretion of calcium and other mineral components from the organism and the sensation of thirst is reduced (Balakhovskiy, 1966). This fact once again emphasizes the need to provide the cosmonauts with water that is complete as to its organoleptic properties and mineral composition.

On the basis of the above, we can assume that it will be necessary in working out methods of artificial mineralization of regenerated water to use the duration of the space flight as the basic criterion. Thus, on short flights we have considered it possible to limit ourselves to adding to the water certain amounts of mineral salts which are primarily responsible for its organoleptic properties. These include, in particular, cations which cause the hardness of water, for example, calcium, magnesium and a number of anions, for example bicarbonates, chlorides and sulfates (Petrov, 1960). However, in the case of moderately long flights and long space flights, it is advantageous to enrich the water with the entire spectrum of necessary mineral compounds found in natural drinking water, including trace elements such as fluorine and iodine, for example. The timeliness of this problem is emphasized by the fact that the problems of long orbital flights, the building of lunar stations and flights to Mars are being discussed in the literature at the present time (Still, 1960; Braun, 1965; Mattson, Hayward, 1966). /153

For the purpose of scientifically establishing a basis for methods of artificial mineralization of regenerated water, it is also necessary to deal with problems of standardizing the nature of the salt substances in it. We

know that at the present time, under natural conditions, no homogeneous physiological standards for salt content in drinking water have been developed as yet. However, the information that we have on this point can be used for the development of appropriate standards for regenerated water (Table 31). Evidently, we must take into account a number of factors that follow from specific conditions. Thus, in many instances, for example when working in spacesuits, there is an increased excretion of sodium and chlorine ions with the perspiration, which can lead to dehydration of the organism and reduce its resistance to g-forces and acceleration (Welch, 1963). Therefore, when working out methods for enrichment of regenerated water, in addition to generally accepted standards for its content of mineral components, it is also necessary in many instances to take into account that the content will have to be increased. Further study of this problem will certainly make it possible to develop physiological standards for the content of mineral compounds in regenerated water as they apply to specific spaceflight conditions. A few works on this subject have been published. Thus, for example, in a work by American authors dealing with this question, attention is drawn to the relatively high upper limits for the content of individual mineral components (chlorides, sulfates, fluorine) in water, while the salts of calcium are lacking at the same time (Slonim, 1967). We cannot agree with the latter finding, inasmuch as extensive scientific experience shows that it is necessary to enrich water with this component (Krotkov, 1959; Marrey, 1961). In conjunction with individual spacecraft, Soviet scientists have also worked out recommendations involving the mineral composition of regenerated water. In developing methods /155
of water enrichment we have been guided in regards to the level of mineral components by a consideration of the conditions that exist in nature. As a sample of the determination of the salt content in regenerated water, we used water from the Moscow water supply (Table 32). In view of the fact that this water is characterized by a relatively low content of the trace elements fluorine and iodine, a higher content of these elements in artificially mineralized water was provided for. Thus, for example, the amount of iodine added to the regenerated water (10-20 micrograms/liter) is characteristic of natural waters in regions where goiter is not endemic (Nikolayev, 1955). The fluorine content in the water was standardized on the basis of the requirements set for drinking water by All-Union State Standard 2874-55.

The investigations of methods of enrichment of water under natural conditions has shown that the latter may be based on the administration of mineral components either in the liquid phase (in the form of a solution), in a solid phase (tablets, filters), or by means of ion-exchange.

The use of concentrated salts for this purpose is of interest because of the convenience with which they are added as well as the possibility of enriching water with practically all necessary components. As a basis for this, a method which we modified and which was originally used by P. N. Paley, based on the separate administration of three salt solutions to water, containing ions of calcium, magnesium, sodium, potassium, chlorine, bicarbonate, sulfate, iodine and fluorine in appropriate concentrations (Shikina, Chizhov et al., 1971). This method was successfully tested by us for regenerating water in a well-known one-year experiment involving three men. In the course of the year, the subjects used water which was enriched and had been regenerated from urine

and condensate of atmospheric moisture; this water corresponded to high hygienic requirements in its organoleptic and physical-chemical parameters (Table 32). It was established that enriched regenerated water had no negative influence in the human organism and promoted the normal course of vitally important organism functions in the course of its prolonged usage.

TABLE 31.* HYGIENIC STANDARDS FOR THE CONTENT OF MINERAL COMPONENTS IN NATURAL DRINKING WATER

| Parameters and concentrations | | Author, year |
|---|---|---|
| Hardness, mg·eq/liter | | |
| Total | 7 | All-Union State Standard 4152-48 |
| | 2—4 | Marrey, Belyayeva (1961) |
| On the basis of calcium bicarbonate | 2—10 | European standards for drinking water quality (1963) |
| Calcium, mg/liter | 75—200 | International standards for drinking water, Geneva (1964) |
| | 100 | Petrov (1960, 1962) |
| | 50—100 | Bokina (1963), Grebenkin, Rakhov (1964) |
| | | Bassharzhiyeva-Taniyeva (1965) |
| Magnesium, mg/liter | 50—150 | International drinking water standards, Geneva (1964) |
| | 30 | European standards for drinking water (1963) |
| Sodium, mg/liter | 200 | Petrov (1960) |
| | | Malezhik (1962) |
| | 250 | Poluektov (1966) |
| Potassium, mg/liter | 2,5—18 | Poluektov (1966) |
| Chlorides, mg/liter | 200—600 | International drinking water standards, Geneva (1964) |
| | 500 | Malevskaya (1958) |
| | 350 | European standards for drinking water quality (1963) |
| | 300 | Drachev (1960), Bokhina (1960) |
| | 100—300 | Petrov (1960), Malezhik (1962) |
| Sulfates, mg/liter | 500 | All-Union State Standard 2874-54 |
| | 200—400 | Bokina (1956), Drachev (1960) |
| | 250 | International drinking water standards, Geneva (1964) |
| | 100—300 | European drinking water standards (1963) |
| | 1,5 | Petrov (1960, 1962) |
| | | All-Union State Standard 4152-48 |
| Fluorine, mg/liter | Optimum | Cherkinskiy, Zaslavskaya (1956) |
| | 0,8—1,0 | |
| | Permissible | Gabovich (1957) |
| | 1,5 | |
| | 1,0 | Aksyuk (1956), Faydysh (1960) |

*Note: Commas indicate decimal points.

TABLE 32.* HYGIENIC EVALUATION OF REGENERATED WATER BEFORE AND AFTER ENRICHMENT BY VARIOUS METHODS

| Parameters | Prior to enrichment | Methods of Enrichment of Water | | | | | | Control (tap water) |
|---|---|---|---|---|---|---|---|---|
| | | Cloth filters | Multi-component solutions | Tablets + dicalcium silicate | Dolomite + fluorite | Gypsum + dolomite + anionite, EDE-10P | Semipermeable membranes | |
| Active pH reaction, un its | 5,0 | 6,0—7,0 | 7,0—8,0 | 7,0—8,0 | 6,0—7,0 | 7,0—8,0 | 6,0—7,0 | 7,0—8,0 |
| Odor, points | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Taste, points | 0 | 0 | 1 | 1 | 1 | 1 | 0 | 1 |
| Transparency, centimeters | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
| Chromaticity, degrees | 5 | 10 | 5 | 5 | 10 | 10 | 10 | 10 |
| Hardness, mg·eq/liter | 0 | 1,5 | 2,2 | 2,5 | 0,8 | 2,9 | 2,8 | 3,0 |
| Calcium, mg/liter | 0 | 15 | 25,7 | 42,6 | 16 | 53,6 | 52,0 | 39,0—44 |
| Magnesium, g/liter | 0 | 2 | 10,2 | 6,8 | 1,5 | 3,4 | 3,1 | 8,5 |
| Chlorides, mg/liter | 6,4 | 0 | 62,5 | 81,6 | 0 | 6,7 | 6,8 | 9,9 |
| Sulfates, mg/liter | traces | 0 | 14,4 | 12,5 | 0 | 20,1 | 20,0 | 25,5 |
| Alkalinity, ml | 0,1 | 0 | 1,9 | 2,2 | 2,1 | 2,1 | 2,1 | 2,3 |
| Oxidizability, mg $O_2$/liter | | | | | | | | |
| permanganate | 4,4 | 4,2 | 3,5 | 5,1 | 1,8 | 1,3 | 1,2 | 3,6 |
| bichromate | 24 | 30 | 24,2 | 42 | 20 | 22,4 | 20,2 | 32 |
| Ammonia, mg/liter | 0,1 | 0,2 | 0,12 | 0,1 | 0,05 | 0,1 | 0,1 | 0,2 |
| Nitrites, mg/liter | 0,02 | 0,04 | 0,025 | 0,017 | 0,012 | 0,025 | 0,01 | 0,03 |
| Nitrates, mg/liter | 0,15 | 0,15 | 0,18 | 0,15 | 0 | 0,1 | 0 | 0,3 |
| Calcium, mg/liter | 0 | 0 | 8,5 | 8 | 4 | 4 | 4 | 4 |
| Sodium, mg/liter | 0 | 0 | 53,5 | 42 | 4 | 4 | 4 | 10,5 |
| Iodine, micrograms/liter | 0 | 15 | 10,0 | 10 | — | — | — | 5 |
| Fluorine, mg/liter | 0,1 | 0 | 1,0 | 1,1 | 0,1 | 0,1 | 0,1 | 0,1 |

*Note: Commas indicate decimal points.

However, in connection with the development of water supply systems for long flights, a need arose to study methods of enrichment of the water, not in the liquid but in the solid phase. This was linked primarily to design requirements and was due to the fact that the use of concentrated mineral solutions meant an increase in the weight of the system and called for the development of special dispensing devices. The development of such a dispensing device that would work reliably would also mean an additional increase of weight and energy consumption for the water supply system. It is interesting in this respect to use water enrichment methods that are based on the addition of salts in the solid phase in the form of solid filtration materials which can be used in the form of a complex layer and can function as the regenerated water passes through it. These substances include certain cloth filters with mineral fillers, natural and artificially synthesized minerals, tablets, ion exchange resins and combinations of the above method /157

Of the available types of cloth filters, we used the "Dializatornaya" and "Bel'king" with mineral fillers having the following composition (in g):

| 1. | | 2. | | 3. | | 4. | |
|---|---|---|---|---|---|---|---|
| $CaSO_4$ | 0.7 | $CaSO_4$ | 0.7 | $CaCO_3$ | 1.5 | $CaCO_3$ | 1.5 |
| NaCl | 1.0 | $NaHSO_4$ | 0.4 | $NaHCO_3$ | 0.4 | $KHCO_3$ | 0.2 |
| $NaHCO_3$ | 0.6 | $KHCO_3$ | 0.2 | $KHCO_3$ | 0.2 | $NaHCO_3$ | 0.4 |
| $CaCO_3$ | 1.5 | $MgCO_3$ | 1.5 | $Mg(OH)_2$ | 0.7 | $CaSO_4$ | 0.7 |

The composition of the first filler was similar to that of a German filter (Senyavin, 1964), while the three others were suggested by us. The studies that were performed showed (Table 32) that the water which was judged best in terms of its hygienic parameters was that which was enriched by using the dialyzing filter containing filler No. 4.

However, the supplies of enriched water turned out to be insufficiently great. Therefore, their practical utilization will only be possible after a basic design has been worked out that takes into account successive replacement of filters or regeneration by reprocessing.

The question of using tablets for conditioning water during space flight is of particular interest because of their small weight and size and the convenience with which they can be added. In conjunction with the low solubility of tablets that contain sulfate and carbonate salts of calcium, giving water its taste and hardness, we proposed tablets that would dissolve easily and which would contain necessary macroelements and trace elements with the exception of calcium: NaCl -- 0.12 g, $KHCO_3$ -- 0.025 g, $MgSO_4$ -- 0.05 g, KI -- 0.00014 g, NaF -- 0.008 g per liter of water.

The addition of calcium was accomplished by passing a volume of water through a layer made of natural or artificial minerals -- gypsum, dolomite, dicalcium silicate, etc. (Shikina, Chizhov, 1971). Regenerated water enriched in this fashion corresponded to all requirements imposed on it in terms of mineral composition.

In conjunction with the conditioning of water, there is also interest in using granulated natural and artificial minerals, placed in a column through which water passes. For this purpose, a number of natural minerals with different chemical compositions have been studied including components necessary for the enrichment of water -- calcium, magnesium, chlorides, sulfates, sodium, potassium, fluorine and iodine. They also include the following minerals and rocks: gypsum ($CaSO_4$), dolomite, $CaMg(CO_3)_2$, calcite ($CaCO_3$), pectolite ($Ca_2NaSi_3O_8$), desmine ($Na_2CaAl_2Si_6O_{16}\cdot 6H_2O$), foyaite ($NaAlSiO_4$ and $NaFeSiO_4$), cancrinite ($NaAlSiO_4\cdot CaCO_3$), nepheline and so forth. The substances containing fluorine include fluorite ($CaF_2$), as well as villiomite (NaF), which /158 occur as inclusions in rocks. For the experiments we selected appropriate granules of minerals, measuring 2-3 mm, selected following preliminary crushing and sifting of samples through metal screens. In choosing the minerals, their solubility under static and dynamic conditions was taken into account, as well as resistance to vibration and other stresses. It was established that the optimum substance in this regard was a complex layer filled with such rocks as dolomite, gypsum, fluorite and other minerals that contained the necessary macroelements and trace elements. As a result of enrichment of water by this method, when water was regenerated from products of human vital activity, drinking water was obtained that was adequate in terms of its organoleptic as well as physical and chemical properties, corresponding to the requirements of the All-Union State Standard (see Table 32). Hence, the possibility of using natural minerals in water supply systems was demonstrated.

A certain degree of interest as far as the development of water conditioning methods is concerned can be found in methods involving its enrichment by means of artificially produced minerals. Those recognized as best included samples of gypsum-magnesium filters which contained $CaSO_4$, CaO, MgO, $MgCl_2$ as well as dicalcium silicate ($CaO\ SiO_2$), obtained by roasting a mixture of ores in a furnace at high temperatures. Water enriched with these minerals corresponded in terms of its organoleptic and physical and chemical properties to the appropriate high hygienic standards. Further efforts aimed at the synthesis of artificial minerals, taking into account the fact that they would include trace elements (F, $I_2$) as well as silver ions for the purpose of simultaneously decontaminating the water, are of particular interest.

It appears promising to use ion-exchange resins for the enrichment of regenerated water. The principle of the method lies in the addition of calcium bicarbonate to the water when solutions of calcium sulfate and calcium chloride are passed through anionite.

We used the sorption characteristics of various samples of anionite (EDE-10P, AV-17) and others at set parameters for the rate of passage of water through the system of the spacecraft. In Table 32 we have listed data that show the possibility of enrichment of water with calcium, chlorine, sulfate and other elements by means of ionites.

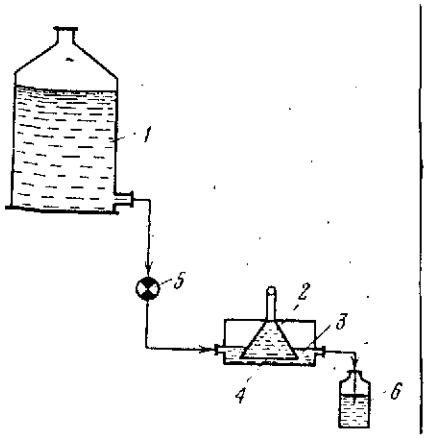



Figure 50. Diagram of Saturation of Regenerated Water with Trace Elements Through a Membrane.
1, Bottle containing distilled water; 2, Funnel with saturated solution; 3, Cell through which water passes; 4, Membrane made of cellophane; 5, Three-way stopcock; 6, Collector for enriched water.

A certain amount of attention centers around the membrane method of mineralization of regenerated water. In a paper by Lukovyy, Shikina and Luzina (1972) the object of the investigation was a cellophane membrane dividing a cell containing enriching salt solutions and regenerated water to be enriched. Thanks to the phenomenon of osmosis, diffusion of mineral components into the water occurred. The degree of artificial mineralization of the water was studied as a function of the concentration and composition of the salt solutions and of the rate of passage of /159 the water through the cell. For this purpose, we studied individual salts of calcium, magnesium and sodium as well as complex salt systems containing both macroelements (calcium, magnesium, sodium, sulfates and chlorides) and trace elements (potassium, sodium, fluorine, and iodine). The system by which the experiment was conducted is shown in Figure 50. The hardness of the regenerated water prior to enrichment of calcium chloride varied from 3.4-40.0 mg·eq/liter with a water throughput range for the system of 18.4-1.45 liters/hour. As the throughput of the water increased, the degree of its mineralization decreased. The optimum hardness of the regenerated water was on the order of 3.4-3.6 mg·eq/liter and was achieved with a water throughput of 18.4 liters/hour. This corresponded to an amount of chlorides in the water of 134-137 mg/liter, corresponding to the requirements of the All-Union State Standard for drinking water. When calcium sulfate was dissolved in the water, its hardness was in the low numbers, on the order of 0.8-0.4 mg·eq/liter. The quantity of sulfates was 14.8-19.2 mg/liter. However, this fell within the corresponding normal limits for natural drinking water. In experiments performed with enrichment of water by salts, magnesium sulfate and sodium bicarbonate separately, it was also established that by regulating the water throughput across the membrane it is possible to achieve addition of these ions to the water in the necessary concentration. Experiments involving the enrichment of water with complex solutions of salts, including macroelements and trace elements, have shown that the addition of multicomponent salt solutions simultaneously to water does not disturb their diffusion through the membrane and the washing out of any individual ions in corresponding concentrations (Lukavyy, Shikina, Luzina, 1972).

As a result of the study, drinking water with high hygienic parameters was obtained. The possibility of using the membrane method for regeneration and conditioning of water under special conditions was demonstrated.

Hence, on the basis of the above, we developed methods of artificial mineralization of regenerated water, with the duration of the space flight taken into account. /160

The proposed system is shown in Table 33. It must be mentioned, however, that this breakdown is of a conditional nature and the choice of one method or another is a function of the specific conditions of the object in question, including a number of requirements of a technological, size-weight and energy nature and so forth.

TABLE 33. METHODS OF ARTIFICIAL MINERALIZATION OF REGENERATED WATER DURING FLIGHTS OF VARYING DURATION

| Brief flights (up to 3 months) | Long flights (up to 1 year or more) |
|---|---|
| 1. In the liquid phase (p-p$CaCl_2$)<br>2. In the solid phase<br>a) Natural minerals (dolomite)<br>b) Artificial minerals (dicalcium silicate)<br>c) Mineral-anionite filter (dolomite, EDE-10P, gypsum-magnesium stone) | 1. In the liquid phase, a complex of salt solutions<br>p-p 1 $mgSO_4$, $NaHSO_4$<br>p-p 2$CaCl_2Ki$<br>p-p 3$KHCO_3$, $NaHCO_3$, NaS)<br>2. In the solid phase<br>a) Natural and artificial minerals including trace elements:<br>- dolomite + fluorite ($CaMg(CO_3)_2$ + $CaF_2$);<br>- dicalcium silicate including F, Ag;<br>b) Minerals combined with tablets having the following composition (in grams):<br>NaCl - 0.12<br>$KHCO_3$ - 0.025<br>$MgSO_4$ - 0.05<br>Ki - 0.00014<br>NaF - 0.008<br>3. Cloth filters<br>4. Semipermeable membranes |

On the basis of the studies we performed, we worked out systems for enrichment of water for a number of spacecraft and tested them both under ground and simulated flight conditions. In addition, the method of water enrichment by means of concentrated salt solutions was also proposed and successfully used with melted glacier water under the conditions of an Antarctic expedition on the drifting station "SP-13" (Il'in, Chizhov, Shikina, 1972).

Hence, summing up the above, we must conclude that for the purpose of giving regenerated water appropriate organoleptic properties, it is advantageous to enrich it with macroelements; on long flights it is also necessary to add trace elements, especially fluorine and iodine, to the water.

Decontamination of Regenerated Water

The problem of decontamination of water in water supply systems for /161
spacecraft is one of the most important problems in its development for both short and long flights. On short flights, the problem of storage of supplies of drinking water aboard a spacecraft is necessarily linked to the development of methods for its preservation which will allow not only a preservation of the chemical composition and its organoleptic properties but also effective methods of preventing the development of microflora in the water in the event of its secondary exposure.

We know that in developing water supply systems based on containers for storage of drinking water, in addition to rigid metal containers, internal, soft, flexible hermetically sealed containers must be used which will allow water to be supplied to a cosmonaut under weightless conditions. In this connection, the development of methods of decontamination of water supply systems for brief flights must take into account the possibility of using a number of structural materials: titanium, duralumin, polymer films, resins and plastics. During the study it was found, for example, that the manufacture of containers intended for storage of drinking water can use such materials as titanium, duralumin, edible resins, teflon film (F26), high-pressure polyethylene and so forth. When they are in contact with water, these materials do not cause organic substances to be given off into it, so that they ensure a reliable and constant decontaminating effect. The need for decontamination of water that has been regenerated from products of human vital activity or as a result of the functioning of onboard technical systems, for example, electrochemical generators, is also dictated by a number of circumstances. We know, for example, that in many instances the original products used for water regeneration may serve as good nutrient media for microorganisms. This is particularly true of urine and the condensate of atmospheric moisture, but may also apply to a condensate which is formed during the functioning of electrochemical current generators. It has been shown, for example, that while the condensate that is formed as a result of the functioning of a hydrogen-oxygen fuel cell has a certain bactericidal effect due to a high concentration of hydroxyl ions, the condensate of a membrane fuel cell will not have the same effect and can serve as a nutrient medium for microorganisms. Hence, when these facts are taken into account, the possibility cannot be excluded that bacteria from the original products will enter the water if the technology for its regeneration breaks down. In addition, there is a danger of secondary contamination of the water in conjunction with the /162
need for developing reliable supplies of drinking water for prolonged spaceflights.

Before moving on to a discussion of methods of decontamination of water during flight, it is necessary to study the quantitative and qualitative composition of the microflora that are characteristic of the original products. For this purpose, for example, we carried out tests to study the microflora of a condensate of atmospheric moisture collected aboard a spacecraft or a pressurized chamber. From a sample of condensates we prepared dilutions of various concentrations (1:10, 1:100) and then carried out

superficial innoculations (0.05 ml each) on solid nutrient media (meat-peptone agar). The microorganisms were counted after two to three days of cultivation in a thermostatically controlled environment with t = 30° by direct counting of the colonies. When the colonies were counted in a dish, a qualitative differentiation in terms of cultural characteristics was simultaneously performed. Experimental data shown in Table 34 show that in the investigated condensates referred to as CAM (Condensate of Atmospheric Moisture) and CFC (Condensate from Fuel Cells) the total numbers for the micropopulation was quite high and varied from 100-150,000 microbes/ml. One can see that the composition of the microflora in all the condensates includes spore-free bacilli which produce colonies that are colored yellow, lemon-yellow and pink, the coccal forms of bacteria that produce colorless colonies, and the quite frequently encountered bacteria of the genera Mycobacterium and Pseudomonas. There were no microflora in condensates that had a pH higher than 10.

The data we obtained are in agreement with the data of authors who have studied the bacterial content of the air in a pressurized cabin in experiments involving human beings. Thus, according to the data of Viktorov (1969), the contamination of the air in a pressurized cabin can vary from several tens to tens of thousands microbial bodies.

It should be pointed out that the considerable variations that occur in the quantitative and qualitative evaluation of microbial populations of condensates of air in pressurized cabins are associated to a large extent with the conditions under which the experiment was performed. Thus, for example, in addition to the flora that are characteristic of the human organism and which enter the air from the oral cavity, nose, surface of the cutaneous coverings (intestinal bacilli, staphylococci, streptococci), the condensate may be found to contain bacteria from the coatings of the inside of the spacecraft, instruments, various coverings and elements that make up the equipment. In addition, we have data which indicate the specific nature of the bacterial flora for closed hermetically sealed objects that are the consequence of a species variability of the microflora of the human organism under these conditions (Viktorov, 1969)

Hence, according to the data of these authors, the condensate of atmospheric moisture is most frequently found to contain staphylococci (78% of the total number of microbes) and Sarcina, which enter from the air. About 18% of the inoculations in the total number of bacteria are diphtheroid. There are /164
a great many γ-negative bacilli of the streptobacterial type, which do not form spores and have point-like colonies that are transparent, coiled, of the type of bacilli found in the throat but not precisely identified. Yeasts and molds enter very rarely while spore forms are practically nonexistent. The bacterium E. coli is found rarely and usually intestinal bacilli are found of the genus Clypsiella, which indicates the specific nature of the microflora in closed hermetically sealed areas.

Hence, the efforts in this direction indicate the need for developing reliable methods of decontamination in a water regeneration system to be used aboard a spacecraft. In order to ensure decontamination of the regenerated water and the associated systems during spaceflight, it is theoretically

possible to use those methods of sterilization as well as preservation discussed above (Chapter II). These include physical (ultraviolet radiation, action of ultrasound and low temperatures, magnetic treatment of the water) and biological approaches (administration of antibiotics and biologically active substances) in addition to chemical ones which involve treating the water with chemical and preservative substances. Each of these methods of decontaminating water being stored in appropriate technical systems made of modern structural materials must be taken into account form the standpoint of its use in space flight.

Physical Water Decontamination Methods

Among physical methods, considerable interest attaches to freezing, but this method of decontamination is widely used only when economic refrigerators are employed or under the conditions of an orientation flight or a spacecraft which makes it possible to use the low temperatures on the dark side. Considerable interest attaches to the use of ultrasound and ultraviolet radiation, since these methods have a lethal effect on microflora with simultaneous oxidation of organic impurities contained in the water. Hence, the use of these methods makes it possible to solve on a complex basis problems of both decontamination and regeneration of water from certain moisture-containing wastes.

We know that ultrasound has a definite biological effect. Thus, for example, small fish and frogs have been observed to be killed near sources of ultrasonic waves and the structure of water plants and microorganisms have been disturbed. There is as yet no single theory explaining the bactericidal action of ultrasound. We know, however, that the basis for all the processes that occur in the area or medium subjected to the sound is the phenomenon of cavitation. When ultrasonic waves travel through an aqueous medium, rapid alternation of compression and decompression is observed. When the intensity of the sound reaches a certain level, negative pressure develops in the medium; /165
a solid medium breaks down, forming cavities into which pores of fluid as well as dissolved gases penetrate. In these areas, a pressure of several tens of atmospheres arises. The bacterial cell is very rapidly broken down under these conditions. In addition, in the opinion of many authors, as a result of exposure of water to ultrasound in the presence of air there may be formation of hydrogen peroxide and nitric acid, which constitute an oxidation-reduction system that has strong oxidizing properties (Levinson, 1962). The more dissolved gases there are in the water, the greater the formation of "bubbles" during its decontamination by ultrasound and consequently the higher the bactericidal effect. A decrease in the bactericidal effect occurs in direct proportion to the increase in the viscosity of the medium being subjected to ultrasound (Grund, Stelter, 1954).

The effects produced by ultrasound are affected to a large extent by the specific properties of the object: size, shape, physiological conditions (Komolova, Levinson, 1961). The most resistant organisms are the microorganisms that have a spherical shape (D'yachenko et al., 1964; El'piner, 1959, 1960). In view of the fact that the study of the bactericidal effect of ultrasonic waves was carried out using devices at various power levels, different frequencies of oscillation, in both open and closed systems, it is very

difficult to systematize all of the data in the literature. However, the majority of investigators feel that in order to achieve decontamination of river water the intensity of the oscillations must be at least 2 W/cm$^2$.

TABLE 34.* CHEMICAL COMPOSITION AND CERTAIN PHYSICAL PARAMETERS OF THE CONDENSATE OF ATMOSPHERIC MOISTURE AND THE MOISTURE OBTAINED FROM ELECTROCHEMICAL GENERATORS

| Parameters, mg mg/l | Maximum permissible concentration | CAM | | CFC | |
|---|---|---|---|---|---|
| | | Maximum | Minimum | Maximum | Minimum |
| pH | 6,5—9,0 | 7 | 6,1 | 10 | 4,45 |
| Ammonia | 2,0 | 160 | 8,6 | 0,52 | 0 |
| Nitrates | 50,0 | 10 | 0,1 | 0,28 | 0,12 |
| Nitrates | 0,1 | 1,25 | 0,1 | 0,025 | 0,007 |
| Total nitrogen | — | 170 | 30 | — | — |
| Phosphates | 0,1 | 2,6 | 0,01 | — | — |
| Calcium | 80—100 | 30 | 0,12 | Traces | 0 |
| Magnesium | 50 | 8,3 | 0,2 | 1,42 | 0 |
| Potassium | — | 2 | Traces | 117 | 0 |
| Sodium | — | 2,5 | 0 | 4,5 | 0 |
| Chlorides | 350 | 350 | 0 | 2,84 | Traces |
| Sulfates: | 250 | 5,68 | 4,8 | Traces | 0 |
| Total hardness mg·eq/l | Up to 7,0 | 5,5 | 0,2 | | 0 |
| Permanganate oxidability, mg $O_2$/l | 5—10 | 114 | 1,5 | 27 | 0,8 |
| Bichromate oxidability, mg $O_2$/l | — | 950 | 7,0 | 88,0 | 6,4 |
| Hydrocarbons | — | 0,01 | — | — | — |
| Diethyl ether | — | 0,4 | 0,01 | — | — |
| Acetaldehyde | — | 2 | Traces | — | — |
| Propionic aldehyde | — | 0,04 | 0 | — | — |
| Acetone | — | 5 | 0 | 1 | Not 0,5 |
| Methanol | — | 2,7 | 0 | 24 | 0,5 |
| Ethanol | — | 342 | 0 | 6 | 0,5 |
| Propanyl | — | 0,3 | 0,15 | — | — |
| Acetic acid | — | 27 | 0 | — | — |
| Propionic acid | — | 1,4 | 0,3 | — | — |
| Oleic acid | — | 3 | 0,2 | — | — |
| Isooleic acid | — | 2 | 0,2 | — | — |
| Capric acid | — | 2,2 | 1,9 | — | — |
| Isocapric acid | — | 0,14 | — | — | — |
| Amines | — | — | — | — | — |
| Total number of bacteria, microbes/ml | No more than 100 | Maximum 1,212,000 | Avg. 168 670 Min. 380 | Max. 1,046,000 | Avg. 151,000 Min. 0 at pH 10 |

*Note: Commas indicate decimal points.

In our studies, we investigated the decontaminating action of ultrasonic oscillations in water from the Moscow water supply which had been artificially contaminated with a culture of the bacterium E. coli, as well as several samples of water regenerated from moisture-containing wastes.

Samples subjected to ultrasound were poured into sterile test tubes with a volume of 20 ml each and placed in a thermostatically controlled ultrasonic generator. Exposure to ultrasound was at a frequency of 800 kHz for 2-4 minutes. Some samples were exposed to sound in closed test tubes, while others allowed air to enter.

The water samples were subjected to artificial contamination by cultures of the E. coli bacterium at the rate of 1,000, 10,000, 50,000 and 100,000/ml. At the end of the exposure to ultrasound the water was used for inoculating a solid medium (Fuchsin-sulfite agar). The cultures were incubated in a thermostatic container at 37° for 24 hours, after which the number of colonies that had grown was counted. Water subjected to artificial contamination was subjected to complete sanitary-hygienic monitoring before and after exposure to ultrasonic vibrations.

The studies that were performed showed that as the contaminating dose increased, the number of viable microflora remaining increased as well. As we can see from the data below, the percentage of deaths of microorganisms, even after two minutes of exposure to ultrasound, was very high (from 87.2 to 93.1): /166

| With a contamination of | After exposure to ultrasound, M ± m | Mortality, % |
|---|---|---|
| 1,000 | 128 ± 43.2 | 87.2 |
| 10,000 | 1,610 ± 375 | 83.9 |
| 50,000 | 3,740 ± 504 | 92.4 |
| 100,000 | 6,764 ± 1,060 | 93.1 |

The results of the tests conducted to determine the action of ultrasound on open and closed test tubes of water with 4 minutes exposure are listed below:

| No. of microorganisms with contamination | In Closed Test Tubes: following exposure, M ± m | In Closed Test Tubes: Mortality, % | In Open Test Tubes: following exposure, M ± m | In Open Test Tubes: Mortality, % |
|---|---|---|---|---|
| 1,000 | 46 ± 3 | 95 | 35 ± 12 | 96.5 |
| 10,000 | 80 ± 5 | 99.2 | 144 ± 31 | 98.5 |
| 50,000 | 173 ± 8 | 99.6 | 204 ± 24 | 99.6 |
| 100,000 | 564 ± 1 | 99.4 | 378 ± 24 | 99.6 |

Increasing the duration of ultrasonic exposure to 4 minutes caused a considerable increase in the death of microorganisms -- up to 95-99.6%. It must be pointed out that all the differences in the ultrasonic effects on microflora in open and closed test tubes are statistically unreliable (t = 0.7; 0.38; 0.56). However, the percentage of deaths of microorganisms was very high (96.5-99.62%).

The results of a sanitary-hygienic study of water subjected to artificial contamination before and after ultrasonic exposure are listed below:

| Parameters | Prior to exposure | After exposure |
|---|---|---|
| pH | 7-8 | 7-8 |
| Odor, points | 0 | 0 |
| Taste, points | 0 | 0 |
| Transparency, cm | 30 | 30 |
| Chromaticity, degrees | 10 | 10 |
| Hardness, mg·eq/liter | 2.5 | 2.0 |
| Sulfates, mg/liter | 24.0 | 24.0 |
| Chlorides, mg/liter | 11.4 | 10.5 |
| Calcium, mg/liter | 16.8 | 16.0 |
| Ammonia, mg/liter | 0.2 | 0.1 |
| Nitrites, mg/liter | 0.03 | 0.03 |
| Nitrates, mg/liter | 0.5 | 0.5 |
| Oxidizability, mg $O_2$/liter | | |
| permanganate | 5.73 | 4.8 |
| bichromate | 25.6 | 15.6 |

As we can see from the data above, there were no significant changes in the hygienic parameters of the quality of water following exposure to ultrasound if we take into account the oxidation of the organs that occurred as the result of the death of active forms of microbes.

Hence, these data indicate a high decontaminating efficiency of the method of ultrasonic exposure. The degree of decontamination is influenced by the duration of the exposure to the sound and the degree of microbial contamination. It has been found that the higher the number of microorganisms in the water, the greater the amount that will remain after exposure to sound. However, the percentage of deaths is practically constant in all cases and very high. /167

The influence of ultrasonic vibrations thereby ensures maintenance of the basic sanitary and hygienic parameters of drinking water with a high bactericidal effect and a simultaneous oxidation of the organic components.

Another physical method of decontamination of regenerated water in such water supply systems is the ultraviolet irradiation method. Interest in ultraviolet irradiation as a decontamination method is explained by its advantages: rapid action and simplicity of execution while retaining the original physical and chemical properties of the drinking water. As sources of ultraviolet radiation, mercury lamps of two types can be used:

1. High-pressure mercury-quartz. The average output of "bactericidal energy" for these lamps is at least 5% of the electrical energy employed (Kul'skiy, 1963). The electrical power of a type PRK lamp is 100 W.

2. Type BUV low-pressure argon-mercury lamp. The output of "bactericidal energy" of these lamps is 14% (Glibin, 1955). The electrical power of these

lamps is up to 30 W. There are two types of apparatus available to irradiate the water: submersible and non-submersible radiation sources. The submersible sources are characterized by a high efficiency of the radiation in comparison to regenerative water supply systems but they are complicated in design. Devices with non-submersible sources are simple in design but some of their radiation is dissipated wastefully due to scattering and absorption by reflecting surfaces. In practice, purification of water in water supplies under terrestrial conditions most generally uses the OV-AK apparatus (Kh-1 with submersible radiation source). We know that the bactericidal effect of physical methods is based on the change in the internal structure of the microorganisms and does not extend to all forms of bacteria, including sporogenic. It has been shown that small doses of ultraviolet radiation can have a positive influence on the growth and multiplication of bacteria. A further increase in the radiation dose will kill them.

We know that the influence of various doses of ultraviolet radiation on the vital activity of bacteria involves the direct photochemical effect which they have on living tissue. Severe disturbances in the structure of the cell and the processes taking place in the latter cause the death of the microorganisms, while insignificant ones may increase its vital activity (Bogdanova, 1957). The author has found that in intermediate doses, with insufficient irradiation, a retardation of vital processes in microorganisms may take place at a certain time. When regenerative systems for water supplies are used, it is necessary to take into account the practice of decontamination of water by using ultraviolet radiation under terrestrial conditions. Thus, for example, decontamination of drinking water by means of ultraviolet irradiation in centralized water supply systems is seeing increased application. /168

The use of devices for ultraviolet radiation has shown that the effect on decontamination of water, in comparison with chlorination, is much higher (Sokolov, 1960, 1964). In order to achieve the required decontamination, it is necessary to have a certain dose of ultraviolet which causes a bactericidal effect and is a function of the qualitative and quantitative composition of the microflora in the water. The initial bacterial contamination must not exceed a coli index of 1,000 (Cherkinskiy, Trakhtam, 1962). The work of Sokolov (1964) established that the amount of energy required for decontamination of water may be established on the basis of the effect of E. coli as the most resistant microorganism.

Studies by the Academy of Communal Hygiene involving the study of the rate of death of E. coli in artificially contaminated water has shown that in order to kill 97-98% of the microbial cells with an original contamination of 100 microbial bodies/ml, an energy of 7,500-90,000 microns/W·sec/cm$^2$ is required. In order to have complete destruction of all of the existing microflora, at least 13,000 microwatts/sec/cm$^2$ of energy are required, while in order to kill 99-99.9% of the original number of spore forms up to 60-72,000 microwatts·sec/cm$^2$ of energy are needed.

V. F. Glibin (1955) succeeded in achieving complete sterilization of water contaminated with E. coli in 5 minutes, with the water 5-50 cm from the reflector. However, further exposure at doses that would ensure total

sterilization of the water could not provide a sufficient guarantee for long storage. In the case of secondary contamination of the water the microorganisms will multiply in it without any difficulty, since ultraviolet radiation has no aftereffects. It is the lack of aftereffects that has been the principal reason why this effective method of decontamination has not been used for water preservation. It must be kept in mind, however, that this method of decontamination simultaneously solves another problem involved in the construction of regenerative water supply systems -- the oxidation of organic impurities in regeneration of drinking water by the photochemical method.

Among the physical methods of decontamination of regenerated water, we must include the effect produced on it by magnetic oscillations. At the present time, many investigators are interested in studying the influence of /169
natural and artificial magnetic fields on water as well as various biological objects, beginning with the simplest microorganism and ending with man. A great deal of interesting data has been collected which indicates that water which contains foreign impurities changes its physical and chemical properties markedly under the influence of the magnetic field (Klasen, 1966; Pressman, 1968). The authors feel that the influence of the magnetic field causes the surface tension, viscosity and electrical conductivity of water to increase, for example, changing its optical density, electrical permeability, and speeding up the coagulation of solid particles as well as the crystallization process. At the present time, there is no one theory for explaining the nature of the processes that occur when water is treated magnetically. There is only a hypothesis which explains the characteristics of active water by changes that occur in the orientation of the nuclear structures of the hydrogen in the water molecule due to the redistribution of the energy bonds. At the same time, there are data which indicate that water which passes through sorbents and ion-exchange resins does not change under the influence of a magnetic field. However, the literature does not contain any data on the influence of magnetic fields on regenerated water.

We know that water will enter any biological system, being a medium in which all vitally important metabolic processes of the cell occur, ensuring the safety of its existence.

Recently, many researchers have reported that "magnetized" water has an influence on the chemical and biological processes of both macro- and microorganisms. A study of the action of magnetized water on man has yielded contradictory results. Some authors mention "acute toxicity", while others claim a favorable effect resulting from the use of magnetized water in diseases of the bile ducts and urinary ducts and in atherosclerosis (Glebov, 1965; Dardymov, Brekhman, 1968). In experiments on animals (Lisin, 1967) it was demonstrated that rabbits which were given magnetized water for 6 months showed no changes in behavior. At the same time, there was a reliable change in certain blood parameters indicating biological activity of the magnetized water (a decrease in sedimentation rate, a rise in leucocytosis, a decrease in the number of eosinophils). Other authors cite a noticeable increase in diuresis as well as inhibition of stone-formation in the animals under the influence of magnetized water (Glebov, 1965). Thus, for example, in mice which had human kidney stones placed in their urinary bladders and were then given 1 ml of magnetized

water daily (in milk) an examination after 30 days showed that the number of crystals formed around the stones was 2.5 times less than in the controls. The morphological studies showed that animals that received magnetized water for 6 months exhibited phenomena characteristic of the stress reaction: hypertrophy of the adrenals, shrinking of the thymus gland, decrease in the weight of the spleen. At the same time, however, the acute toxicity of the magnetized water /170
in experiments on mice was approximately equal to the toxicity of distilled water. Thus, in the case of intraperitoneal administration of water that had been treated with a constant magnetic field with a strength of 1,000-1,500 oersteds the $LD_{50}$ was 3.5 ml at 20 grams of animal weight. In view of the fact that none of the experimental animals that were given magnetized water for a long time (6 months) died, and in view of the considerable pathohistological changes that were found, the authors conclude that water treated with a magnetic field has definite biological activity and its toxic effects are manifested only moderately (Glebov, 1965; Dardymov, Brekhman, 1963). The literature lacks any data on the influence of magnetized regenerated water on the organism, but the facts cited above should be taken into account in discussing the problem of using a magnetic field to process water in a water-supply system for spacecraft. It is necessary to take into account the positive characteristics of this method; simplicity of its structural execution with low energy consumption and the development of a decontaminating effect on the water in this method, with a possibility of oxidation of the organic impurities in it. In this connection, we consider it necessary to dwell in somewhat more detail on this method of decontamination of water, it being the one most suitable for the functioning of regenerative water supply systems.

An analysis of the data in the literature indicates that under certain conditions (frequency, wavelength, original concentration of microbial bodies, exposure) magnetic waves have a pronounced bacteriostatic and bactericidal effect (Gliban, 1952; Schastnaya, 1958; Brown and Morrison, 1954-1956). Attempts were made to find the mechanism of the influence of the magnetic irradiation on the biochemical structures and physiological functions of various strains of staphylococcus, streptococcus, Proteus vulgaris, and B. subtilis (Pavlovich, 1968; Schastnaya, 1958). However, the mechanism of this influence has not been clarified in final form. Some investigators (Vaydrakh et al., 1961) feel that there is no other influence other than heat acting on the biological object in a magnetic field. Other researchers have obtained results which cannot be explained simply by a thermal effect. Thus, Brown (1965) found that under the influence of a magnetic field with a frequency of 65-600 Hz the viability of E. coli was decreased sharply. Segnin and Castelain (1947) and Segnin (1949) observed the action of a magnetic field with a frequency of 14,000 mHz on a culture of staphylococcus and E. coli. The culture was heated to 34° for one minute, and cessation of multiplication of bacteria was observed. Schastnaya (1958) studied the effect of ultrahigh frequency electromagnetic waves on a culture of E. coli and Staphylococcus aureus, keeping the temperature of the suspension between 37 and 42°, i.e., below the level that is lethal for these bacteria. The growth of colonies in magnetized cultures was less than in cultures that were heated in a water bath to the /171
same temperatures.

Nyrop (1946) reported that E. coli died 5-10 seconds after exposure to a magnetic field of 205 W/cm when the medium was heated to 40°, while with ordinary heating this effect was observed only at 60° after 10 minutes. Regardless of the interpretation of the biological effect, the magnetic field has a definite bacteriostatic and bactericidal effect on microorganisms without considerable energy expenditure.

It was appropriate to present the results of some data that were obtained by us in experimental studies involving the magnetization of water. In this work we used a one-day culture of E. coli (strain 671) whose viability after magnetization was checked by surface (0.01 ml of solution) inoculation on Endo agar (pH 7.3-7.4). The culture was kept at 37° for 24 hours. Concentration of microbial cells was determined by means of an FEK-56 photoelectrocolorimeter and simultaneously by inoculation on Endo agar. The colonies were counted on the second, fifth and tenth days of the experiment. The control was composed of nonmagnetized cultures of E. coli.

The study of the influence of the electromagnetic field in experiments was performed by us as a function of the concentration of the microbial suspension, the intensity of the magnetic field and the nature of the substrate under investigation. The original substrate for this study was tap water and distilled water, as well as a condensate of atmospheric moisture characterized by the following parameters: permanganate oxidability 0.6 mg $O_2$/liter, bichromate oxidability 133.76 mg $O_2$/liter, $NH_3$ -- 67; $NO_2^-$ -- 1.8; $NO_3^-$ -- 0.38; $Ca^+$ -- 14.8; $Cl^-$ -- 23 mg/liter. The original microbial levels in the solutions under test were 10,000, 50,000 and 100,000 microbes/ml. The water throughput in the magnetic device varied from 50 to 500 ml/hour. The intensity of the magnetic field at the time that its effect on water was studied was 500-1,000-1,500 oersteds. The tests were performed on devices of two types for creating a constant electromagnetic field. The circuits of these devices are shown in Figure 51 and 52.

Theoretically, device 2 differed from device 1 in having a single passage of the water through the magnetic line of force and a considerably shorter contact time between the water and the magnetic field. The results obtained are average data from 5 similar tests. In the following we have listed the characteristics of the magnetic fields of the two devices:

| Device 1 | | | Device 2 | | |
|---|---|---|---|---|---|
| Current Strength, A | Voltage, V | Strength of magnetic field, oersteds | Current Strength, A | Voltage, V | Strength of magnetic field, oersteds |
| 1.0 | 12.0 | 500 | 0.5 | 6.0 | 3,500 |
| 1.5 | 17.0 | 1,000 | 1.0 | 14.0 | 5,750 |
| 2.0 | 20.0 | 1,500 | 1.5 | 20.0 | 7,500 |
| | | | 2.0 | 26.0 | 8,250 |
| | | | 2.5 | 32.0 | 8,750 |

In device 1, there is the following relationship between the survival of the microorganisms (microns/ml) and the strength of the magnetic field: /172

| Strength, oersteds | Microbial level, microbes/ml | | |
|---|---|---|---|
| | 10,000 | 50,000 | 10,000 |
| 500 | 0 | 13 | 400 |
| 1,000 | 0 | 1 | 200 |
| 1,500 | 0 | 0 | 0 |

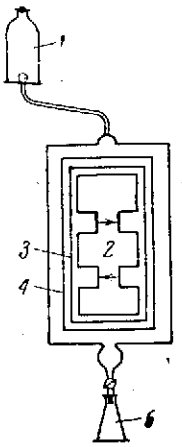



Figure 51. Electromagnetic Device for Decontaminating Water (Type 1). 1, Container for water; 2, Core; 3, Housing; 4, Space; 5, Receiver for decontaminated water.

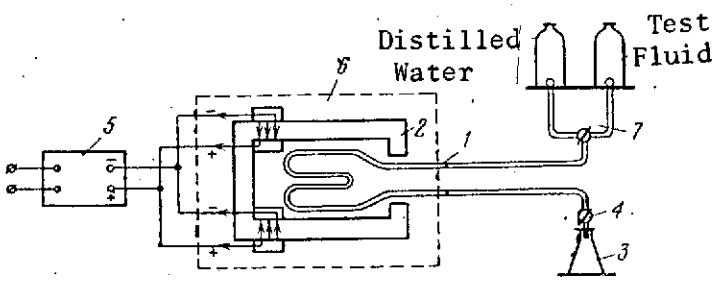



Figure 52. Electromagnetic Device for Decontamination of Water (Type 2). 1, Glass tube through which water passes; 2, Electromagnet; 3, Receiving flask; 4, Stopcock to regulate flow of fluid; 5, VSA-5A rectifier; 6, Electromagnetic device; 7, Stopcock for controlling the "distilled water-test fluid" system.

As we can see, in a device of the first type with the strength of the magnetic field equal to 1,500 oersteds, total inactivation of bacterial cultures is accomplished. At a voltage of 500 or 1,000 oersteds the viability of the bacteria is inversely proportional to the original concentration of microbial cells. In a suspension with a smaller concentration, the effect of magnetization is greater. Obviously, in a suspension with a large concentration of microbial bodies there will be a "shielding effect"; this is confirmed by the data of other authors (Schastnaya, 1950). Investigation of the dependence of the viability of the microorganisms on the rate at which the water passes through the magnetic device has shown the following:

| Water throughput ml/hour | Number of Microorganisms | | |
|---|---|---|---|
| | 10,000* | 100,000 | 1,000** |
| 50 | 0 | 0 | 0 |
| 100 | 0 | 0 | 22 |
| 500 | 50 | 64 | 43 |
| 1,000 | 81 | 100 | 100 |

*Microbial level at a strength of 1,500 oersteds. **Same, at 1,000 oersteds. /173

It has been found that the maximum decontaminating effect is observed at a minimal water throughput (50 ml/hour), indicating that as the contact time increases the magnetizing effect increases as well. In the decontamination of regenerated water using magnetic device 2 the following data were obtained:

| Strength, oersteds | Number of microorganisms (in microber/ml) with a microbial level of thousands of microbes/ml | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | I | | | II | | | III | | |
| | 10 | 50 | 100 | 10 | 50 | 100 | 10 | 50 | 100 |
| 500 | 0 | 0 | 0 | 0 | 0 | $5 \cdot 10^3$ | 0 | 0 | 0 |
| 1,000 | 0 | 0 | $2 \cdot 10^3$ | 0 | 0 | $5 \cdot 10^4$ | 0 | 0 | $7 \cdot 10^3$ |
| 1,500 | 0 | 0 | $2.5 \cdot 10^3$ | 0 | 0 | $1.4 \cdot 10^4$ | 0 | 0 | $6.4 \cdot 10^3$ |

Note: I - for a water throughput rate of 50 ml/hour
II - for a water throughput rate of 100 ml/hour
III - for a water throughput rate of 500 ml/hour

In a suspension containing 10 and 50,000 cells per ml, total death of microbial cells is achieved at all investigated throughputs and magnetic field strengths. In a suspension with a concentration of 100,000 microbial bodies per ml at the same throughput, total death of the microorganisms was obtained only at a strength of 500 oersteds, while at strengths of 1,000 and 1,500 oersteds growth of viable cells was observed, although to a much lesser degree than in the controls. This result is somewhat different from the data obtained in device 1, where a direct relationship between the bactericidal effect and the magnetic field strength was observed. As far as the dependence of the survival of magnetized cells on water throughput is concerned, the result obtained in working with the first device was confirmed to the extent that the effect increased as the throughput decreased. The inverse relationship between the decontaminating effect and the density of the microbial suspension was confirmed, as we mentioned earlier. A matter of considerable interest as far as confirming these data is concerned is measurement of the temperature and the pH of the solution at the input and output of the device. The water temperature before and after magnetization was measured using a mercury thermometer and the reaction of the solutions (pH) was recorded on a Type pH-340 pH-meter. Measurements were conducted at time intervals of 5 minutes, 30 minutes, 1 hour and 2 hours following magnetization. In order to clarify the influence of the electrolytic composition of the original solution on the process of magnetization we performed parallel studies involving measurement of pH only on distilled and regenerated water, but also with addition of an electrolyte to the water (at the rate of 0.5 g NaCl/liter) and also in a simulated condensate of atmospheric moisture. This was interesting because the available data indicate that distilled water which does not contain duplicate ions does change its physical and chemical characteristics, including pH, under the influence of a magnetic field. The data obtained are shown in Table 35.

/174

TABLE 35.* INFLUENCE OF MAGNETIC TREATMENT OF WATER FOR VARYING PERIODS OF TIME (IN MINUTES) ON THE pH OF THE MEDIUM

| Strength, oersteds | Distilled | | | Regenerated | | | | Regenerated + NaCl | | | | Condensate | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 5 | 30 | 60 | 5 | 30 | 60 | 120 | 5 | 30 | 60 | 120 | 5 | 30 | 60 |
| Control | 6,00 | 6,42 | 5,9 | 6,9 | 7,0 | 7,25 | 7,3 | 7,15 | 7,3 | 7,38 | 7,4 | 9,2 | 9,07 | 9,9 |
| 500 | 7,0 | 7,3 | 7,07 | 7,1 | 7,3 | 7,45 | 7,5 | 7,25 | 7,28 | 7,4 | 7,45 | 9,4 | 9,25 | 10,1 |
| 1000 | 7,5 | 7,7 | 7,7 | 7,6 | 7,5 | 7,7 | 7,7 | 7,27 | 7,29 | 7,34 | 7,35 | 9,4 | 9,3 | 10,1 |
| 1500 | 7,5 | 7,5 | 7,59 | 7,7 | 7,5 | 7,59 | 7,52 | 7,24 | 7,27 | 7,31 | 7,35 | 9,4 | 9,22 | 9,3 |

*Note: Commas indicate decimal points.

These tests revealed that the pH of water changes insignificantly under the influence of magnetic processing. A tendency toward a slight increase in the pH factor of the medium with an increase in the magnetic field strength was observed but these variations lie within the limits of measurement error. It should be pointed out that in the case of a culture of E. coli the optimum pH is 6.5-7.5, and a pH of 9.0 (as in the condensate which was studied) has an unfavorable effect on E. coli.

At the same time, the temperature studies we conducted showed a considerable difference between the data obtained on device 1 and device 2. While the water that had passed through device 2 showed no temperature variations before and after the experiment, the temperature of the water that passed through the first device rose from 22° to 48-64° following magnetization. Similar temperature effects were seen by many authors and treated as one of the factors in the lethal effect of magnetic fields on bacteria. We know that the temperature optimum for the vital activity of E. coli lies within rather narrow limits, t = 34-36°, but there are papers which indicate that at t = 40-45° the E. coli bacillis retains its survivability. The absence of heating of the water in device 2 evidently explains its lower decontaminating effect on water under the same conditions. However, in this case, with microbes in the water, there was a considerable decontaminating effect, which indicates a specific action of the magnetic field on the water. Thus, for example, a magnetic field /175 with a strength of 1,500 oersteds reduces the number of bacterial cells in aqueous suspensions by about 8 times in comparison with an original suspension which contains 10,000 microbes/ml. With a high concentration of cells in the original suspension (50,000) the effect of the magnetic field is less pronounced, especially in tap water where the number of viable cells is decreased by only a factor of 2, and in regenerated water by a factor of 9. The data we obtained are in agreement with the opinion of many authors, for example, P. I. Schastna (1968), who note that simple heating of a bacterial suspension does not produce the same effect as heating the same suspension in a magnetic field. Hence, the study which we performed indicated the theoretical possibility of using a magnetic method of treating water for the purpose of decontaminating it during spaceflights. In addition to the physical methods of decontaminating water, which we have studied above, there is considerable interest in freezing, but this method obviously can only be used in orientation flight of spacecraft, where it is possible to use the natural cold of the dark

side of the craft. In this connection, it will obviously be possible to use solar energy, but the solution of the problem lies in the future.

It should be pointed out that the studies we have carried out in this regard show that water has retained its physical-chemical and bactericidal properties in the solid phase for several months. Among biological methods that have been used thus far for decontamination of regenerated water, an important place is occupied by treatment with antibiotics. However, the recommendation of this method for long periods of time will obviously be determined not only by its bactericidal effect but also by the influence on the organism as a whole, which will require careful study in this regard.

At the present time, chemical methods of preservation and decontamination of water using various chemical compounds and preservatives is of the greatest importance. Among these, the most important (as we have already pointed out) are the solutions of ionic silver which have come into extensive usage in systems designed for water supplies based on reserves on brief space flights. However, on long flights a problem arises involving the use of regeneration systems for water supplies in terms of developing a method of decontaminating the water as it flows through, using decontaminating agents not in the form of solutions but in the solid phase. This is due first of all to the fact that the addition of a preservative to the regenerated water in the form of a solution considerably complicates the design of the special dispenser. The development of such a reliably working system requires additional increases in weight and energy consumption. It is interesting to use for this purpose solid filter materials and sorbents (charcoal, ionite, impregnated cloth) which have bactericidal properties and can be installed in the system as complex layers /176 and can function as the water to be cleaned flows through them. Sources in the literature mention several ways of decontaminating drinking water which are based on the bactericidal properties of the ions of heavy metals: silver, copper, mercury and so forth (Rubtsov, 1968; Mestrobeany, Paunensen, 1960) and on the use of solid filtering materials such as ion-exchange resins and activated charcoal (Lalli, Orlandi, 1952; Shtannikov, 1964; Rotman, 1960; Markaryan, 1955; Grigor'yeva, 1967). The use of the latter is advisable for the purposes of simultaneously decontaminating the water and freeing it from mechanical and chemical impurities. We know that several ion-exchange resins that are used in water regeneration systems simultaneously act as active bacterial filters (Nikitinskiy, 1926; Adamov, Noskov, 1962; Shtannikov, 1964).

Thus, Adamov and Noskov suggested that by filtering water artificially contaminated by microbes of typhoid fever and E. coli through KU-1 cationite, the microbial content was decreased 99.8-100%. However, the possibility of secondary contamination by filtration through ionites was not excluded.

In our work, we dealt with the problem of studying the decontaminating effects of the following solid filter materials: ionites -- KU-2×8 ($H^+$); KU-2×8 ($Cu^{++}$); KU-2×16 ($H^+$); KU-2×16 ($Cu^{++}$); AV-17 ($OH^-$); charcoal -- saran, AG-5, ash-free saran and saran in the $Ag^\circ$-form. In addition, we studied natural materials: dolomite, fluorite, villiomite, dolomite in the $Ag^\circ$-form. Columns containing sorbents had tap water passed through them which had been infected with a one-day culture of E. coli at a concentration of 100,000

cells/ml. The concentration was determined on the FEK-56. The latter was checked by using a culture on Endo nutrient medium. The columns and the water were sterilized prior to infection with intestinal bacilli. The volume of the sorbent in the swollen state was 10 ml. The filtration rate was 50 ml/hour. From the tests of the filtrate that was obtained a number of dilutions ($10^{-1}$, $10^{-2}$) were prepared and used to make inoculations of 0.05 ml each on Endo nutrient medium. The colonies were counted after 24 hours and then, as we mentioned earlier, the results were converted for 1 ml of filtrate. We recorded the number of samples of filtrate that were completely purified by the sorbent to remove bacteria as well as the time in which the bacterial count returned to the original pollution level.

The hygienic problem of using ionites for improving the quality of water requires study not only of the interaction of the sorbent with the bacteria but also a determination of the possibility of a practical utilization of resins for decontaminating water to get rid of these pathogenic agents. The sorbents have bactericidal properties, so that in the case of using regenerated water directly for drinking (if reserves are not produced and there is no need /177 to have a decontamination unit), sorbents allow reliable bactericidal purification.

In the following we have listed comparative data on the capacity of various sorbents with respect to E. coli from which it is clear that the investigated cationites in the $H^+$ form and the anionite in the hydroxyl form have the same bacterial capacity:

| Sorbent | Purified Filtrate, ml | Sorbent | Purified Filtrate, ml |
|---|---|---|---|
| Cationites | | Charcoal | |
| KU-2-8 ($H^+$) | 3,550 | AG-5 | 3,200 |
| KU-2-16 ($H^+$) | 3,400 | Saran | 2,350 |
| KU-2-8 (in the Cu form) | 4,200 | Saran ash-free | 2,200 |
| KU-2-16 (in the Cu form) | 8,250 | Saran (Ag) | 22,400 |
| | | Minerals | |
| Anionites | | Dolomite | 900 |
| | | Dolomite (Ag) | 34,200 |
| AV-17 ($OH^-$) | 3,600 | Fluorite | 350 |
| | | Villiomite | 800 |

Thus, one volume of KU-2×8 ($H^+$), KU-2×16 ($H^+$) and AV-17 ($OH^-$) gives respectively 350, 340 and 360 ml of purified filtrate. It should be pointed out that the curve of the dynamics of sorption of E. coli on AV-17 anionite has a phase of total sterility in which the amount of sterile filtrate is 50 ml (Figure 53). Total sterility of the filtrate is evidently explained by a change in the active reaction of the medium so that pathogenic cells which have an amphoteric nature are fixed by sorbents at high pH values (Shtannikov, 1964; Valdevets, 1966).

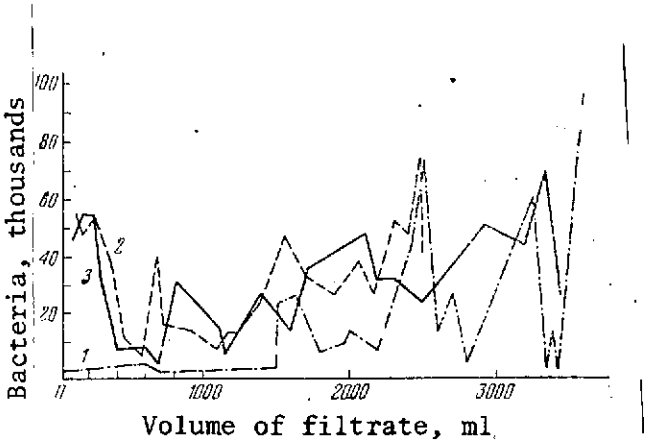



Figure 53. Dynamics of the Sorption of E. coli on Activated Charcoal and Anionite. 1, Anionite AV-17 in the OH -form; 2, AG-5 charcoal; 3, Saran charcoal.

The bacterial capacity of the cationites in the copper form is 1.5-2.0 times higher than in cationites in the hydrogen form (Figure 54). It is possible that the high purifying effect of these cationites in the copper form is explained by the decontaminating action of copper ions (Frobisher, 1962; Mesrobeany, 1960).

We know that silver ions in the fluid phase are used as a solution or as silver ions applied to sorbents for decontamination and preservation of water. In our work we studied the comparative bacterial capacity of activated charcoal (AG-5, saran, ash-free) and the same kind of charcoal in the silvered form. It was found that the bacterial capacity of saran charcoal in the silvered form is 10 times greater than activated charcoal, whose capacity is the same as the capacity of the cationites in the ($H^+$) form. The investigated minerals gave a lesser effect in terms of protection against E. coli bacteria than did the sorbents listed (Figures 55, 56). However, following silvering of the minerals (dolomite) this effect increased sharply (the amount of purified filtrate increased 38 times). One is struck by the alternating nature of the curves of the dynamics of the sorption of E. coli in which a phase of sterility of the filtrate alternates with phases in which the contamination rises. /178

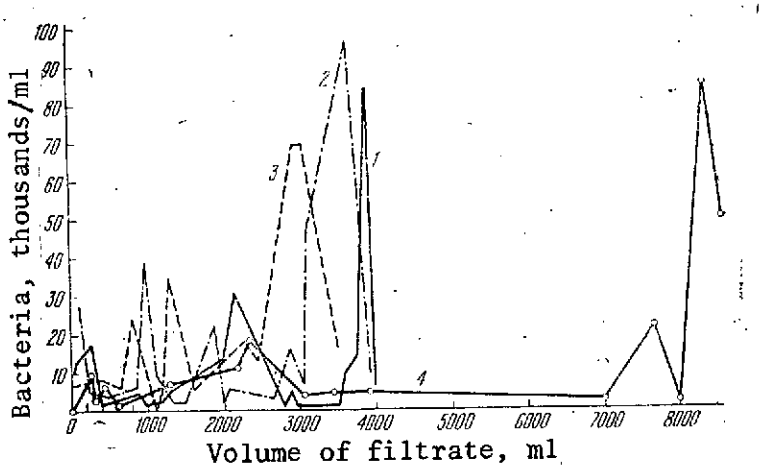



Figure 54. Dynamics of the Sorption of E. coli on Cationites KU-2×8 (1) and KU-2×16 (2) in the H-form, KU = 2×8 (3) and KU-2×16 (4) in the Si-form.

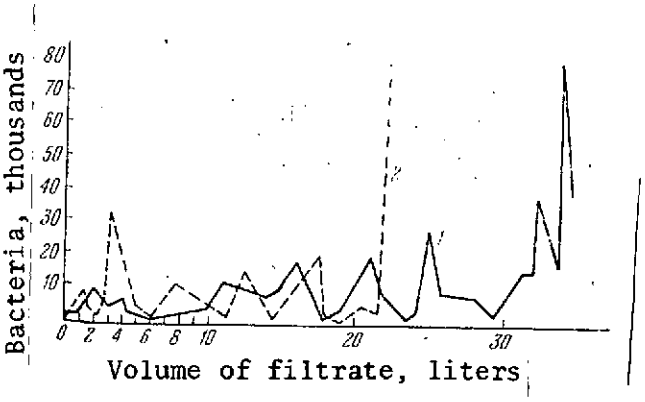



Figure 55. Dynamics of the Sorption of E. coli on Silvered Sorbents. 1, Dolomite (Ag°); 2, Saran charcoal (Ag°).

Hence, these data indicate the promising possibility of using these sorbents not only for purification but also for decontamination of water in space. For this purpose, we are also interested in the problem of studying the bactericidal properties of certain cloth filters impregnated with the salts of heavy metals. A special antimicrobial cloth was used as the cloth filter. It is a silver salt of the grafted copolymer of cellulose and polymethacrylic acid which contains 4% silver. /180

In order to obtain "antimicrobial" cloth, cotton cloth modified by the addition of polymethacrylic acid was treated for 30 minutes at 20° and at a vat ratio of 50:1 with an aqueous silver nitrite solution (10% of the weight of the cloth).

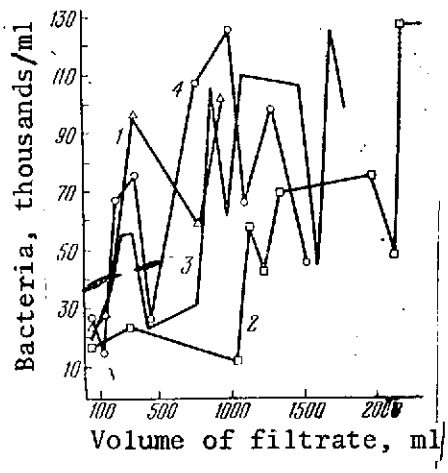



Figure 56. Dynamics of the Sorption of E. coli on Minerals. 1, Fluorite; 2, Ash-free; 3, Dolomite; 4, Villiomite.

To study the factors that influence the washing out of the silver from the cloth, filtration with tap water was carried out through filters having an area of 9.6 $cm^2$ at varying rates. The total volume of water filtered in the various experiments was 5.0-8.0 and 10.0 liters.

To study the possibility of decontamination and preservation of drinking water by filtration through cloth filters, artificial contamination of tap water with cultures of E. coli 675, B. staphylococcus 209 and B. anthracoides in amounts of 10,000 microbial bodies/ml was carried out. The tap water was dechlorinated prior to contamination. The total volume of contaminated water was 10 liters. Filtration of the water was carried out in two stages. First of all, 5 liters of water were filtered, after which samples were taken for quantitative determination of the silver and inoculations on nutrient media were made to isolate microorganisms.

The inoculations of samples contaminated with intestinal bacilli were carried out using Endo and Levin media. Quantitative analysis of B. anthracoides staphylococci were performed by inoculation on meat-peptone agar. Then the remaining 5 liters of water were filtered to determine the same parameters. The water filtration rate was 0.66-0.5 liter/minute. The filtered samples were kept in the dark at room temperature. Determination of the silver concentration and the amount of microorganisms were performed later, after 1, 3, 6, 24 and 96 hours had elapsed since filtration. In addition to quantitative analysis of the microorganisms, there was also selective microscopy of individual colonies, as well as study of the fermentative activity of the isolated cultures. Determination of the fermentative activity of E. coli bacteria was performed by inoculation on the following sugars: lactose, glucose, maltose, mannite and saccharose. To study the cultures of staphylococci, the nature of their growth on bouillon and gelatin and the decomposition of carbohydrates were determined. Later, for each liter of filtered fluid, the decrease in concentration was 0.02 mg/liter on the average. In experiments with artificial inoculation with E. coli of tap water that had been dechlorinated, the average concentration of silver following filtration of the first 5 liters was 0.148 mg/liter. After filtration of the remaining 5 liters it was 0.034 mg/liter; consequently, there was a more rapid death of microorganisms in the first test. Thus, while in the first sample the average number of intestinal bacilli immediately after filtration was 386 microbial bodies/ml, in the second it was 11,000 microbial bodies/ml. However, if we study these same samples one hour later, we find that in both samples the viable E. coli bacteria were unable to divide, while in the control sample of water, stored without preliminary filtration through cloth filters, the number of E. coli bacteria remains at a high level. /181

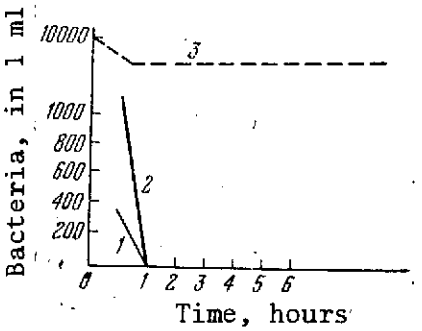



Figure 57. Death Rate of E. coli Following Filtration of Water Through Cloth Filters.
1, Test I; 2, Test II; 3, Control.

On the graph shown above we have presented data on the death of intestinal bacilli in water samples following filtration through cloth filters (Figure 57). These same water samples were later stored for 96 hours after filtration. Inoculations with microorganisms made every 24 hours showed that no viable E. coli bacteria could be found during this period of storage. Hence, even a silver dose of 0.034 mg/liter has a reliable bactericidal effect.

Data from the physical-chemical analysis of the water showed that following filtration through cloth filters, and in the course of storage, properties did not change. However, the possibility of practical utilization of bactericidal cloth filters in a water supply system will obviously depend to a large extent on the development of appropriate designs which will make it possible to replace filters as they wear out.

# CHAPTER V: MEDICAL AND BIOLOGICAL EVALUATION OF REGENERATED WATER

## Characteristics of the Sanitary and Hygienic Monitoring of the Quality of Water Regenerated from Moisture-Containing Wastes

As we have already pointed out, sources of water aboard a spacecraft may include the products of human vital activity, moisture which is formed during the operation of a number of technical systems, and (aboard future spacecraft) moisture from plant life. Naturally, monitoring the quality of the water which is regenerated from these products will be determined primarily by their chemical composition. /182

It must be assumed that as they develop the optimum technological reserves for the functioning of each regenerative system, researchers will necessarily be interested primarily in those problems associated with the creation of conditions that will ensure that the water to be regenerated lacks any undesirable impurities, especially substances that could affect the living organism in any way. In this connection, a distinction will be made in these studies between water obtained from specific original products and the method of its evaluation.

Of course, the basis for the study of regenerated water must be a system of methods that are widely employed in water-supply practice, corresponding to the needs of nationwide and international standards. However, the generally used methods which characterize the quality of water must employ additional tests involving consideration of the chemical composition of the specific product being used for regeneration.

Let us examine some of the characteristics of monitoring the quality of water which is obtained under specific conditions from unusual raw materials for the functioning of regenerative systems in hermetically sealed areas in spacecraft.

As we have already pointed out, the condensate of atmospheric moisture which is formed in the cabin differs markedly in its chemical composition from perspiration and water vapor that are contained in the air expired by man.

We know that the condensate of atmospheric moisture contains practically all of the chemical compounds that are contained in the cabin atmosphere as well as impurities that are formed as the result of the destruction, pyrolysis and hydrolysis of materials from which the equipment of the spacecraft is made (Clemedson, 1959). Thus, for example, it has been shown that the condensate of atmospheric moisture may contain considerable amounts of technical impurities that are not characteristic of the excretion of man through the skin or lungs. It has also been demonstrated that these impurities mainly consist of organic impurities which do not contain nitrogen. As a rule, these organic substances, which are difficult to oxidize, belong to the class of alcohols, aldehydes, ketones, ethers, hydrocarbons and other compounds. /183

Obviously this fact must be taken into account in developing methods of purifying the condensate of atmospheric moisture and methods of monitoring the quality of the water regenerated from it. In this connection, first of all, studies of water obtained from the condensate (aside from the permanganate method) must necessarily involve a determination of the bichromate oxidability which makes it possible to determine a wide range of compounds that are difficult to oxidize. In specific studies, it is sometimes necessary to employ the method of iodate oxidability which makes it possible to oxidize practically all of the organic impurities found in the condensate.

In addition, it is necessary to study and identify a number of impurities whose entrance into the water cannot be ruled out under unfavorable regeneration conditions. In this connection, we must make extensive use of chemical-analytical and particularly chromatographic methods of determination of alcohols, aldehydes, ketones and other classes of chemical compounds in the aqueous phase.

The raw material which is second in importance for the regeneration of water (taking the water balance of man into account) is urine.

We know that human urine contains about 100-150 compounds of both an organic and inorganic nature. The organic compounds make up about 60% and the inorganic ones about 40% of the dry residue. It has been established that many of these substances exhibit a certain degree of toxicity for the organism. Thus, for example, the nitrates which are formed when urine is allowed to stand, upon entering the organism with the drinking water in concentrations of 10 mg/liter or more, cause the disease known as metahemoglobinemia (Kapanadze, 1963; Subbotin, 1958, 1961).

In addition, urine has been found to contain large amounts of certain organic compounds, microbes, and certain enzymes and hormones which are biologically active compounds (Bauer, 1953). It should be pointed out that under the conditions of closed hermetically sealed volumes the composition of the urine undergoes qualitative and quantitative changes and one of the characteristic features of the composition of urine under these conditions is an increase in the specific amount of organic compounds of a nitrogenous nature in it, for example uric acid, urea, ammonium nitrate, etc. It is natural that as we examine questions relating to regeneration of water from urine and its sanitary and hygienic evaluation, we will be forced to use a broad range of hygienic controls as set forth in this chapter to determine the nature of the organic and inorganic components -- urea, ammonium nitrate, nitrates, nitrites, potassium, sodium, calcium, magnesium, chlorine and so forth. The methods of determining the amounts of these compounds are set forth in the appropriate sections.

Among the characteristics of evaluation of water regenerated from urine, /184
especially for long spaceflights, we must include for example the determination of steroid hormone content, which we performed using a highly sensitive biochemical test by the Krekhova method (Krekhova, 1960).

One of the characteristic features of sanitary and hygienic monitoring of the quality of regenerated water is the possibility of using it at levels of oxidability that are in excess of permissible standards. Therefore, if we know the nature and type of impurities that enter the regenerated water, we can evaluate them individually.

For example, when regenerating water from the condensate of atmospheric moisture, alcohols which are difficult to absorb (particularly ethanol) may enter the regenerated water, thereby increasing its oxidability. In this case, it is obviously advantageous to stop using such water, so that the result is a simplification of the water supply system and a reduction in its equivalent weight (Kryuchkov et al., 1972).

A number of characteristics of the sanitary and hygienic evaluation of the regenerated water come to light when we install a system for operational control aboard a spacecraft. Thus, it may not contain a great many tests that are used under terrestrial conditions. Obviously, the principal factors in this respect will be the following: 1) organic compounds, 2) mineral impurities, 3) bacterial contamination. In determining the organic compounds it is possible to use for example the chromatographic, luminescent and several other methods. In some cases, an analysis to determine the presence of organic compounds should advantageously be aimed at one of the most toxic substances. The mineral portion of the water can be checked by a widely employed method such as the conductometric method. However, the use of the conductometer under spaceflight conditions has distinctive characteristics. In view of the integral nature of this method, it is difficult to determine which component causes a given electrical conductivity. For example, regenerated water which contains 10 mg/liter of chlorides, sulfates, calcium, magnesium and exhibits a certain degree of electrical conductivity will be considered potable, while water which contains only 3 mg/liter of ammonia and is characterized by reduced electrical conductivity will be rejected, although the conductometer will give a signal that indicates that the water is potable.

## Sanitary and Hygienic Evaluation of Regenerated Water

It is natural that the recommendations of the method of regeneration and conditioning in a given water supply system can be used only following careful hygienic studies of concentrated regenerated water, intended for human consumption. It is necessary to exclude the possibility of contamination of the water by a number of toxic substances that go to make up the raw products or are involved with the technology by which the water is obtained. We know for example that under unfavorable conditions water which is regenerated from urine and condensate may contain impurities that are characteristic of the original products. As we have already shown previously, most of these components are either toxic or not indifferent to the organism. In addition, the water may contain substances that are used in the course of its regeneration. Thus, for example, some films of synthetic origin or ion-exchange resins which are used for purification may give off chemical substances into the water which cause deterioration of its properties (Shtukovskaya, 1960, 1962; Shtannikov, 1961). In particular, substances such as chlorine and hydrogen peroxide have been employed for obtaining water from a condensate by the

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absorption method with preliminary oxidation. According to the data of Batarova (1965), for example, the amount of hydrogen peroxide remaining in water, if it is above 0.6-0.7 mg/liter, will have a negative effect on hemopoiesis and will cause pathological changes in animals.

On the basis of the above, taking into account the unusual nature and origin of the artificially regenerated water, it becomes necessary to study it from many aspects and in detail. We know that in such cases it is advantageous to use a number of methods of hygienic monitoring (Cherkinskiy, 1960, 1964; Yelizarova, 1922; Rylova, 1964; Pravdin, 1960). These include organoleptic, chemical and biological studies of regenerated water, taking into account the toxicological experiments on animals and on man as well.

## Methods of Sanitary and Hygienic Evaluation of Regenerated Water

In the course of developing a number of methods for regeneration of water from moisture-containing products, the question has arisen of the possibility of using it for drinking and preparation of food. For a sanitary and hygienic evaluation of regenerated products, it is necessary to select those parameters whose determination would constitute a necessary and reliable check of the quality of drinking water under terrestrial conditions and aboard a spacecraft. According to current concepts, sanitary and hygienic evaluation of the quality of water is carried out by methods that include determination of a number of organoleptic, chemical, bacteriological and toxicological parameters. However, a number of these evaluative methods which current sanitary and hygienic experts have at their disposal, involving evaluation of water from normal sources, will be insufficient for a total understanding of the quality of water regenerated from human waste products that contain moisture and water obtained from technical systems. In this connection, a need has arisen for developing /186
a broader range of evaluative methods, including many chemical and biochemical tests which will allow determination of the quality of water obtained from human urine, condensate of atmospheric moisture and other waste products, with a high degree of objectivity. Unlike the methods of hygienic control used in general practice, dealing with the evaluation of regenerated water will necessarily involve the development of a number of appropriate measures that will entail consideration of the characteristics of the composition of the raw materials under spaceflight conditions. Table 36 shows a sample of a physical, chemical and toxicological evaluation of samples of regenerated water. It should be pointed out that in each individual case the characteristic features of the method and the technological process of regeneration were considered and additional methods were employed to determine the specific impurities, and particularly sensitive methods of toxicological evaluation of the water on living organisms were used. The final stage in the study, of course, is a program of research with human participation under conditions of complex utilization of life-support systems in spacecraft simulators.

In the following, we shall discuss several methods of organoleptic and physical chemical evaluation of regenerated water that are most frequently employed in our field. We know that the degree of pollution of water by chemical compounds and its taste characteristics are closely linked (Petrov, 1960). In this connection, in addition to the generally accepted methods of

organoleptic evaluation of water using the point system set forth in the All--Union State Standards (All-Union State Standard 3351-46), a more differentiated analogous method according to Bronshteyn has been employed (1956). The evaluation of the water by the testers was performed using a special questionnaire. Thus, water samples regenerated from CAM apparatus and urine by methods of absorption and vacuum distillation before and after conditioning were approved. As a control, distilled water and water from the Moscow water supply system were used. The temperature of the water to be tested was constant (+25°). It is natural that evaluation of water regenerated from such multicomponent fluids as urine, condensate of atmospheric moisture and the development of methods of water conditioning has made it necessary to make wider use of methods of determination of its content of chemical compounds of mineral origin. The total hardness, potassium and magnesium were determined on the basis of the generally accepted method of complexometric titration with trilon B (All-Union State Standard 4141-48). Murexide was employed as the indicator in the determination of potassium; chromogene blue was used to determine magnesium.

In addition to the chemical-analytical methods based on volume titration, particularly in the development of methods of water enrichment, highly accurate and modern methods of investigating its mineral composition were used as well. These included, for example, flame photometry and photoelectrocolorimetry /188
(Lur'ye, 1963; Vinogradova, 1966). Thus, the determination of potassium and sodium in water was performed using the elvi-650 [sic] flame photometer. The basis of the method consists in the spectrophotometry of the gases which are formed when these elements are burned in a low-temperature flame of illuminating gas (Poluektov, 1966). The chlorides in the water were determined by the Mohr method by titration of a sample of silver nitrate in the presence of potassium chromate (AUSS 4245-48). The analysis of the sulfates in the water was conducted both by the generally accepted method of complexometric titration with trilon B in the presence of black chromogen (Lur'ye, 1963) and by photoelectrocolorimetry on the FEK-M instrument with a yellow filter (Vinogradova, 1966). This method was based on the production and photometry of a stable suspension of barium sulfate in a gelatin solution. The total alkalinity was determined in all cases by titrating it with a standardized solution of hydrochloric acid with phenolphthalein indicator. In view of the fact that the development of a number of methods of conditioning water provides for the presence in it of trace amounts of fluorine and iodine, it was necessary to select the most modern methods of determination. Thus, together with the alizarine zirconium method specified by the All-Union State Standard for the determination of fluorine in water (AUSS 4386-48) (Drachev, 1960), iodine determination was carried out by the volume method according to Pavlova (1964). The essence of this method consisted in the possibility of determining iodine in water in insignificant concentrations on the order of 5-10 micrograms per liter with high accuracy (±3%). The basis of this method was the oxidation of the iodide ion by bromine water with subsequent titration of the extracted iodine with thiosulfate in the presence of starch. It was advisable to include among the analytical methods the determination of residual chlorine and hydrogen peroxide, checking for the presence of these substances in the water used from the CAM, employing a solution of hydrogen peroxide or active chlorine as the oxidizer (Chizhov, 1965, 1966). The basis of the iodometric method of

determination of residual chlorine in water was the reaction involving the extraction of iodine by active chlorine from a solution of potassium iodide (AUSS 2919-45; Drachev, 1960).

To determine hydrogen peroxide in water, the method of permanganatometry was used; this method is based on the use of the oxidizing-reducing properties of the substance (Babko, 1962). Determination of ammonium nitrate, nitrates and nitrites was carried out in water using the generally accepted colorimetric method on the FEK-M (Drachev, 1960; Savchenko, 1961). In carrying out the bacteriological analysis of the water, the number of bacteria per milliliter of water was determined on the basis of the number of colonies that grew in meat-peptone agar in 24 hours with t = 37° (AUSS 5216-50). Due to the possibility of the entry of organic impurities into the water that was regenerated from urine and condensate, the research method included a determination of the permanganate and bichromate oxidability (AUSS 4595-49; Savchenko, 1961) as well as the products of oxidation of nitrogenous organic substances -- ammonium nitrate, nitrites and nitrates (Savchenko, 1961; Lur'ye, 1963). Determination of bichromate oxidability was dictated primarily by the need to have a check on the presence of impurities in the water that were difficult to oxidize (alcohols, aldehydes, ketones) which may be present in the event that the processes for purification of the condensate on sorbents break down. Studies in our laboratory (Ivanova, 1965) have shown for example that the method of bichromate oxidability, in contrast to the permanganate method (according to Kubel'), provides the most objective estimate of the content of impurities of a non-nitrogenous nature in water and particularly in the condensate. In determining the bichromate oxidability, a specially developed semiautomatic device, the "bichromator," was used. /189

To determine the organic impurities, we also used spectral analysis, chromatography and the luminescence method.

The luminescence method of analysis is considered to be one of the most simple and sensitive, but the simplest organic substances do not possess significant luminescence in the visible range of the spectrum. It is true that some luminesce in the ultraviolet region of the spectrum, but this poses certain technical difficulties for the use of these luminescence properties. Attention has been directed to the phenomenon of extinction of luminescence by the interaction of the simplest organic substances with the luminescent dyes uranyl, eosin, rhodamine and uranyl sulfate. The ability of organic substances to luminesce or extinguish the luminescence of dyes is proportional to their concentration; this was used as the basis of the method of analysis used for determining the organic impurities in water. Using the luminescence method, the organic impurities were determined specifically in low alcohols (Karyakin, 1971). As the luminescent dye, a 0.01% aqueous solution of uranyl sulfate was proposed; its luminescence spectrum is a broad, nearly unstructured band with a peak at $\lambda$ = 517.

In the presence of alcohol the luminescent intensity of an aqueous solution of uranyl decreases significantly as a function of the concentration of alcohol. The phenomenon of extinction of luminescence by alcohol is explained by the fact that the uranyl group is bound with two molecules of

water which react not only with the uranium but also with the oxygen in the uranyl group. The interaction with alcohol involves resolution, which causes a change in the probability of electron transitions as a result of the stronger bonds between the components. The sensitivity of the method is $10^{-2}$%. In determining acids, the same phenomenon of extinction of luminescence of a 0.01% aqueous solution of uranyl sulfate is used. The strongest extinguishing effect is produced by acids which possess the highest constant of dissociation. The mechanism of the extinguishing effects also consists in resolution and a change in the probability of electron transitions. The sensitivity of the method is $10^{-5}$%. It is possible to determine acetone in the water by using its ability /190
to extinguish the luminescence of uranyl (fluorescein sodium salt). Extinction occurs only under the stimulating effects of ultraviolet light. It is necessary to take into account the blocking effect of acids in the determination of acetone. Irreversible extinction of luminescence of dyes by acetone in an aqueous solution probably takes place because of oxidation-reduction processes. In this case, the stimulating effect of ultraviolet light is evident. The sensitivity of the method is $10^{-8}$%.

Aqueous solutions of complex organic substances, which are products of the processing of waste products of human vital activity and a biocomplex, can be checked on the basis of their specific luminescence spectra. By means of the luminescence method, based on the recording of the spectra of the intrinsic luminescence of complex organic substances, it is possible to choose an extracting agent for removing organic substances from aqueous solutions. Thus, the best solvent for extracting organic compounds from the culture fluid of chlorella is ether, which selectively extracts organic substances with maximum luminescence at 450 nm, leaving the organic compounds with maximum luminescence at 490 nm in the aqueous solution. Chloroform extracts all of the luminescent organic substances at once, with a maximum at 480 nm. The luminescent method makes it possible, by comparing the spectra, to evaluate the absorption purification of organic substances by activated charcoal. For purposes of hygienic monitoring of the quality of regenerated water, researchers have also studied the possibility of using conductometric methods of determining its content of impurities. The use of this method is obviously promising as far as the development of systems for automatic monitoring of the quality of regenerated water under spaceflight conditions is concerned. The conductometric method is based on the ability of an aqueous solution to change its electrical conductivity as a function of the concentration and nature of the ions present in it. The use of this method for purposes of evaluating the quality of water is valid if we compare the contents of inorganic and organic impurities. The dependence of electrical conductivity on the chemical composition of water containing organic and inorganic components has been established. Work has been performed to provide a basis for using the conductometric method for evaluating the quality of water obtained by the method of vacuum distillation and oxidation-catalytic methods in our regeneration system. The principal impurities, which exceed the permissible standards and constitute a danger to human health, are ammonia, organic substances, nitrites, nitrates, and chlorides in water regenerated by the oxidation-catalytic method.[2] The influence

[2]Without supplementary sorption purification.

of each component of the impurity in the change in the electrical conductivity /191
of the regenerated water was studied. An analysis of the data which were obtained indicates that ammonia, nitrites and nitrates, due to the considerable degree of dissociation and mobility of the ions, have a greater influence on the specific electrical conductivity than the organic substances which are present in thw water being studied. The greatest influence on the electrical conductivity of the solutions under study within the limits of permissible concentrations is exerted by the ions of ammonium. Thus, the electrical conductivity is determined primarily by the increase in the ammonia concentration, but the influence of other ions must be taken into account as well. An analysis of the data obtained has shown that there is no linear relationship between the concentrations of ammonia, organic substances and electrical conductivity of the solution; in other words it is practically impossible to provide a quantitative estimate. However, the abrupt change in electrical conductivity which has been observed makes it possible to develop a signalling device designed to operate at a selected threshold value. This constitutes one of the advantages of this method, making it possible to provide, instead of data on the concentration of individual components, an integral signal to indicate the quality of the water -- whether it is "pure" or "polluted", thus facilitating the observations that must be made by the cosmonauts and simplifying the processing and transmission of the telemetric signal, freeing it of superfluous information. Therefore, when the conductometric method is employed, it is necessary to establish the limit of specific electrical conductivity which corresponds to the maximum permissible level for chemical composition of the drinking water. An analysis of the data obtained has shown that the maximum value for electrical conductivity is $9.5 \cdot 10^{-5}$ $ohm^{-1}cm^{-1}$. If the specific electrical conductivity is higher than the maximum value, the water will not correspond to the sanitary and hygienic requirements imposed by the appropriate All-Union State Standards.

On the basis of these data, a commercial device has been built which signals excess amounts of impurities; it has been used in tests with actual equipment.

Hence, the conductometric method which has been developed for monitoring the quality of water constitutes a successful instrumental solution which is convenient in its application and has sufficient accuracy to ensure that the water will be of a quality which meets the sanitary and hygienic criteria established by the All-Union State Standards.

## Hygienic Evaluation of Water Regenerated by Low-Energy Consumption Methods From Moisture-Containing Wastes

### Hygienic Evaluation of Water Purified by the Sorption Method

Tables 37 and 38 show data from the hygienic evaluation of water regenerated by the sorption method from a condensate of atmospheric moisture as well as moisture obtained from an electromechanical generator before and after its enrichment with mineral components. It follows from these data that in all /194
cases the water regenerated by the sorption method is a colorless, highly

transparent fluid containing an insignificant quantity of organic impurities. Water regenerated from a condensate of atmospheric moisture and fluid from an electrochemical generator using KU-2 resin contained practically no chemical compounds; its composition resembled that of distilled water. However, when water was purified using AV-17 resin in the form of ($SiF_6$), it was found to contain a high content of fluorine, which reached 21 mg/liter. After the water was enriched, its fluorine content fell to 8 g/liter due to the interaction with the calcium chloride added to the water and the resultant precipitation of the compound calcium fluoride, which is difficult to dissolve. Hence, on the basis of these data, we can see that as a rule the composition of regenerated water resembles that of distilled water. However, this water may contain individual chemical components which must be taken into account in selecting the optimum technology for its purification and in its subsequent conditioning. It follows from the data in the tables that following enrichment of the water with mineral components its composition is characterized by high hygienic parameters and meets all requirements imposed on it. The use of appropriate methods of decontamination thus ensured a reliable bactericidal effect. Finally, it may be said that this sorption method of purifying CAM and CFC fluid has made it possible to obtain drinking water with the required qualities, in turn allowing its use for further toxicological experiments on animals.

Hygienic Evaluation of Water Regenerated by the Membrane Method from the Condensate of Atmospheric Moisture

Table 39 shows data from the hygienic analysis of water that was regenerated by the membrane method from a condensate using cellophane and a special film 100. As we can see from the data, the use of this method of purification allowed a significant reduction of the content of products of organic origin and phosphates in the water. Thus, for example, the parameters of oxidability in the water fell from 35 and 160 to 27-24 mg $O_2$/liter, i.e., by approximately 1.3 times for the cellophane membrane and by about 6-7 times when film 100 was used. Hence, the studies showed that there was a considerably greater efficiency on the part of the second type of membrane (film 100) in comparison with cellophane. However, the oxidability of water regenerated by this method exceeded the permissible All-Union State Standard. The data obtained indicate that additional purification using sorbents by this method will definitely make it possible to obtain water of the required quality. However, it will be possible to recommend the membrane method of water regeneration for a water-supply system aboard a spacecraft only after appropriate toxicological tests of this water have been performed on animals. /195

Hygienic Evaluation of Water Regenerated From Highly Concentrated Solutions

In the above we have examined the hygienic evaluation of water regenerated from low-concentration solutions which are products of human vital activity or are formed as the result of the functioning of technical systems. However, as the duration of the flight increases, it will become necessary to carry out a more complete recycling of the water, whose second usage will involve the use of such highly concentrated solutions as for example human urine, water used

for sanitary, living and culinary purposes. The second characteristic to be taken into account in the development of water supply systems for long space flights is the possibility of a repeated usage of water that is produced by higher and lower plants. In this connection, drinking water must be obtained from water of transpiration from higher plants as well as from the condensate or fugate formed as a result of the functioning of a reactor containing unicellular algae. In addition to the characteristics of the chemical composition of the original products and in view of the special characteristics of the methods of their hygienic evaluation mentioned above, it is necessary to study carefully (from the medical-biological standpoint) such energy-consuming methods of regeneration as lyophilization, vacuum distillation, catalytic oxidation and several others. /196

Hygienic Evaluation of Water Regenerated From Urine by the Lyophilization Method

The lyophilization method is worthy of attention particularly since it allows water to be purified by using the vacuum of space and the cold outside the spacecraft without any considerable loss of heat energy.

Experiments that have been performed to develop a method for regenerating water from urine by using lyophilization, taking into account the basic technological parameters, have been described earlier (see Chapter III).

Table 40 shows the data from sanitary and hygienic studies of water regenerated from urine by using the method of lyophilization at various temperatures in an evaporator and condenser with preliminary cooling or heating of the original product, as well as by self-freezing. It follows from the data in the table that the lyophilization method makes it possible to obtain water from urine that contains a minimum amount of impurities.

In experiments with preliminary freezing of urine, the temperature of the latter in the evaporator fell to -10, after which the evaporators were connected to a device and subjected to a vacuum. However, the preliminary freezing of the original product did not produce a higher degree of water purity. This is supported in particular by data on the ammonia content of water regenerated by this method; it was 13-14 mg/liter, while in experiments without preliminary cooling of urine the ammonia concentration in the water was 0.6-4.3 mg/liter. The quantity of organic impurities (as determined on the basis of permanganate oxidability) did not differ markedly from available values in the majority of other methods of water purification. In the case of regeneration of water by another system (with self-freezing), when preliminary freezing was not carried out, there was an intensive boiling of the urine during the initial stage of vacuum processing. After 20-30 minutes, the urine was observed to freeze, after which the regeneration conditions were similar to the above. The process of water regeneration from urine with self-freezing of the raw product took place at temperatures between -10 and +15° in the evaporator and -15 to -78° in the condenser (see Table 40). The data presented in the table on the study of the quality of the water show that the lyophilization process involving self-freezing of the raw products provided a higher degree of purification of the water than when preliminary freezing of the urine was performed. Thus,

for example, the ammonia concentration in water purified by the self-freezing method was 4 to 5 times less than in water which was obtained with preliminary cooling of the raw product. A particularly high degree of purity of the water was achieved by using the self-freezing method at evaporator temperatures of 10-15° while the condenser was at -10 to -15°. Under these conditions, the ammonia concentration in the water was no higher than 1.5 mg/liter and its oxidability (permanganate) was 5.3 mg $O_2$/liter. /198

An important shortcoming of these systems is the length of the process. In order to increase the output of the regeneration system, heating of the evaporator flask was employed, using water baths with temperatures of +30° to +40°. In this case, the length of the process was 4-5 hours, and, as we can see from Table 40, the chemical composition of the regenerated water was significantly better in terms of its hygienic parameters. Considerable practical interest attaches to studies involving the regeneration of water from urine using the lyophilization method under conditions which exclude the elimination of the dry residue from the evaporator. The execution of the regeneration process in this case would have made it possible to cut down on the losses of air which are unavoidable when the dry residue is removed and would considerably simplify the design of the regeneration apparatus. It was necessary to ascertain how continuous prolonged operating cycles for the device would influence the sanitary and hygienic parameters of water that was obtained from urine. Experiments involving the regeneration of water from urine without removing the dry residue from the evaporator were performed in the following order. 500 ml of urine were placed in the evaporator, which was then cooled to 5° to reduce foaming. The evaporators were then connected to a device that subjected them to a vacuum; after the urine had frozen, the evaporator flasks were placed in a water bath at a temperature of 25-30°. When each experiment was over, the flask containing the dry residue was placed in a refrigerator and stored at 0 to +5° until the next experiment. In each successive experiment, 500 ml of urine were added to the flask containing the dry residue of previous experiments and the regeneration process was repeated. The total duration of the experiment was 11 days, with the apparatus operating 3-5 hours a day. It must be pointed out that as the dry residue accumulated the time required to remove the water from the urine increased as well. While during the first experiments the regeneration of 500 ml of water consumed 3 hours, it later took 5 hours.

Table 41 shows data on the sanitary and hygienic evaluation of water that was regenerated from urine by the lyophilization method with a long, continuous operating cycle of the regeneration apparatus. It is clear from the data in the table that the water regenerated in experiments that are repeated many times over without removing the dry urine residue are characterized by relative constancy of composition and contain relatively small amounts of impurities.

Hence, on the basis of the experimental studies that have been performed, it was shown to be possible to regenerate water from urine by the lyophilization method. This method makes it possible reliably to extract water from urine and may be viewed as a promising method for the construction of onboard water supply systems. Water which has been regenerated in this fashion without preliminary purification is characterized by a much smaller amount of /199

impurities of organic and inorganic origin in comparison with the vacuum distillation method. The use of appropriate sorbents and mineral enrichers made it possible to confer properties on this water that would bring it up to the standards demanded by the All-Union State Standards (see Table 41).

On the basis of these studies, an experimental regenerating device was built. The results of tests conducted on an experimental lyophilic apparatus confirmed conclusions previously reached regarding the possibility of obtaining water with high hygienic properties from urine. /200

In conclusion it should be pointed out that the authors conducted a great many tests involving regeneration of water by the lyophilic method from a great many moisture-containing products of human vital activity and from biocomplexes. Thus, for example, the lyophilization method was used to extract water from feces, water used for sanitary and culinary purposes, the fugate from chlorella reactors and other impurities.

These studies also showed the possibility of reclaiming water from these products. The latter indicates that there is some promise to the method of lyophilization for recycling water in the event of inclusion of the plant system in the life-support complex, as well as the system for mineralization of waste products for the purpose of obtaining a nutrient medium for those plants. All of this suggests construction of systems for water regeneration on the basis of the lyophilization method on long spaceflights.

Sanitary and Hygienic Evaluation of Water Regenerated by the Vacuum Distillation Method

A diagram of a system and the conditions for performance of experiments involving regeneration of water from urine by the vacuum distillation method were set forth in the appropriate section. The results of the test that were performed, characterizing quality on the basis of the principal hygienic parameters at various evaporation and condensation temperatures for water regenerated from urine, are shown in Table 42. The vacuum in all of the experiments was 30 mm Hg. Water obtained in all of these modes was transparent and colorless. In Experiments 1 and 6, a slight, scarcely perceptible odor of ammonia was detected.

In order to establish the optimum temperature conditions for evaporation and condensation of water in the vacuum distillation system, we analyzed data from a hygienic evaluation of water that was obtained at temperature intervals in the evaporator from 20 to 50° and in the condenser from 5 to 20° (see Table 42). It should be taken into account that one of the basic parameters indicating the degree of purity of the water obtained from urine was the nitrogen from ammonia, for example. As we can see from the data in the table, at 20° in the evaporator the ammonia indicators in the regenerated water reached high values, on the order of 130-200 mg/liter, while increasing the temperature of the evaporator to 30° caused a considerable drop in the ammonia in the water to 0.14 mg/liter. However, a further increase of the evaporator temperature to 50° led to a new increase in ammonia concentration to 2-4 mg/l. The latter evidently can be explained by the penetration of particles of urine or molecules of ammonia into the water due to excessively violent boiling at these temperatures.

TABLE 36. LIST OF METHODS OF ORGANOLEPTIC, PHYSICAL, CHEMICAL AND BACTERIOLOGICAL EVALUATION OF ENRICHED REGENERATED WATER

| Parameters | Units of measurement | Method of determination | Accuracy of measurement, % | Bibliographic Source |
|---|---|---|---|---|
| Odor | Points | Five-point system | | AUSS 3351-46 |
| Taste | Points | Five-point system of evaluation | | AUSS 3351-46 |
| | | Using the Bronshteyn system | | Bronshteyn, 1956 |
| Chromaticity | Degrees | Cobalt-platinum scale | | AUSS 3351-46 |
| Transparency | cm | Snellen type | | AUSS 3351-46 |
| pH | | pH determination | ±3 | Drachev, 1960 |
| Total hardness | mg·eq/liter | Complexometric titration with trilon B | ±5 | AUSS 4151-48; Drachev, 1960 |
| Calcium | mg/liter | Ditto | ±5 | AUSS 3688-47; Drachev, 1960 |
| Magnesium | mg/liter | Complexometric titration with trilon B | ±5 | AUSS 3820-47; Drachev, 1960 |
| Chlorides | mg/liter | Volume titration with a standard solution of silver nitrate | ±4 | AUSS 4245-48 |
| Sulfates | mg/liter | Complexometric titration with trilon B | | Lur'ye, 1963 |
| | | Photoelectrocolorimetry | | Vinogradova, 1966 |
| Residual chlorine | mg/liter | Iodometry | ±4 | AUSS 2919-45; Drachev, 1960 |
| Hydrogen peroxide | mg/liter | Permanganatometry | ±4 | Babko, 1962 |
| Total alkalinity | mg/liter | Volume titration with a standard solution of hydrochloric acid лоты | ±3 | "European standards for the quality of drinking water", Geneva, 1963 |
| Potassium | mg/liter | Flame photometry ния | ±3 | Poluektov, 1966 |
| Sodium | mg/liter | Ditto | | "International standards for drinking water," 1964 |
| Iodine | mg/liter | Volume titration with a standard solution of sodium thiosulfate | ±3 | Pavlova, 1964 |
| Oxidizability | $O_2$, mg/liter | Permanganatometry | ±3 | AUSS 4595-49; Drachev, 1960 |
| | | According to Kubel' | ±3 | Drachev, 1960 |
| | | Biochromate | | Drachev, 1960 |
| Ammonium nitrate | mg/liter | Photoelectrocolorimetry | ±4 | Savchenko, 1961 |
| Nitrates | mg/liter | Ditto | | |
| Nitrites | mg/liter | Ditto | | |
| Coli titer | | Counting of colonies on meat-peptone agar | — | AUSS 5216-50 |

TABLE 37.* HYGIENIC EVALUATION OF WATER REGENERATED BY THE SORPTION METHOD FROM A CONDENSATE OF ATMOSPHERIC MOISTURE (M ± m)

| Parameter | In a 1-year experiment | | In a "Voskhod" mockup | | Control (tap water) |
|---|---|---|---|---|---|
| | 1 | 2 | 1 | 2 | |
| Active reaction, pH | 4,0±1,0 | 7,0±1,0 | 4,0±1,0 | 7,0±1,0 | 7,0±1,0 |
| Odor, degrees | 0 | 0 | 0 | 0 | 0 |
| Taste, degrees | 0 | 1 | 1 | 1 | 1 |
| Transparency, cm | 30 | 30 | 30 | 30 | 30 |
| Chromaticity, degrees | 5±1 | 5±1 | 5±2 | 5±2 | 5±3 |
| Hardness, mg·eq/l | 0 | 2,12±0,3 | 0 | 3,08±0,6 | 1,8±1 |
| Calcium, mg/l | 0 | 25,6±0,7 | 0 | 50,7±1,3 | 39,6±5,0 |
| Magnesium, mg/l | 0 | 10,2±1,1 | 0 | 6,6±0,4 | 8,5±2,1 |
| Chlorides, mg/l | 6,3±1,1 | 62,5±3,2 | 0 | 85,2±11 | 9,9±8,1 |
| Sulfates, mg/l | traces | 14,4±1,1 | 0 | 28,5±0,9 | 22,5±5 |
| Alkilinity, ml | 0,1±0,05 | 1,9±0,4 | 0 | 2,5±0,09 | 2,1±0,3 |
| Oxidizability, mg $O_2$/l | 1,4±0,1 | 1,5±0,2 | 7,2±0,07 | 7,3±0,03 | 3,5±0,3 |
| permanganate | 23,7±1,2 | 24,2±1,1 | 36±3 | 37±2 | 32±40 |
| bichromate | 0,1±0,03 | 0,12±0,04 | 0,1±0,04 | 0,1±0,05 | 0,2±0,05 |
| Ammonia, milligrams/liter | 0,02±0,005 | 0,025±0,003 | 0,02±0,005 | 0,025±0,003 | 0,03±0,01 |
| Nitrites, milligrams/liter | 0,15±0,003 | 0,18±0,01 | 0,3±0,01 | 0,35±0,02 | 0,3±0,1 |
| Nitrates, milligrams/liter | 0 | 8,5±0,9 | 4 | 4 | 4 |
| Potassium, milligrams/liter | 0 | 53,5±1,2 | 0 | 110±5,0 | 10,5±5,1 |
| Fluorine, milligrams/liter | 0,1±0,02 | 1,0±0,1 | 0 | 1,0±0,1 | 0,1±0,02 |
| Iodine, milligrams/liter | 0 | 10,0±2,0 | 0 | 7,3±3,0 | 5,0±1,0 |
| Microbial contamination, microbes per liter | 0 | 0 | 0 | 0 | 0 |

*Note: In all cases, the water was enriched with solutions of ionic silver (1 milligram/liter): 1, before and 2, after enrichment.

Note: Commas indicate decimal points.

TABLE 38.*| HYGIENIC EVALUATION OF WATER REGENERATED BY THE SORPTION METHOD FROM THE FLUID FROM AN ELECTROCHEMICAL GENERATOR

| Type of sorption purifier | | Parameters (M ± m), milligrams per liter | | | | |
|---|---|---|---|---|---|---|
| | | Total hardness, milligrams·eq/liter | $Ca^{++}$ | $Mg^{++}$ | $SO_4^{--}$ | $Cl^-$ |
| KU-2 resin | I* | traces | traces | 0 | 15,3±0,8 | 2,4±0,4 |
| H+-form | II | 3,1±0,2 | 52,9±5,0 | 5,1±0,3 | 20,1±0,6 | 106,5±3,0 |
| AV-17 resin | I | traces | traces | 0 | traces | 7,1 |
| $OH^-$ form | II | 1,5±0,1 | 30,7±4,0 | 5,4±0,5 | 5,8±0,3 | 38,5±9 |
| Control (tap water) | | 1,8±1,2 | 39,6±5,0 | 8,5±2,1 | 22,5±5,0 | 9,9±3,1 |

| Type of sorption purifier | | (M ± m), mg/l | | | | | |
|---|---|---|---|---|---|---|---|
| | | $F^-$ | $Ag^+$ | Oxidizability, mg $O_2$/l: permanganate | Oxidizability, mg $O_2$/l: bichromate | $NH_3$ | $NO_2^-$ |
| KU-2 resin (H+-form) | I* | 0 | 0,8±0,1 | 1,3±0,9 | 26,8±2,0 | 0,5±0,07 | 0,0175±0,004 |
| | II | 1,2 | 0,8±0,1 | 1,3±0,5 | 27,1±1,9 | 0,5±0,05 | 0,0175±0,005 |
| AV-17 resin $OH^-$-form | I | 21 000±3000 | 0,1±0,05 | 1,18±0,03 | 29,3±2,0 | 1,1±0,1 | 0,045±0,009 |
| | II | 3 000±1000 | 0,09±0,02 | 1,6±0,05 | 30,1±3,0 | 1,2±0,09 | 0,05±0,01 |
| Control (tap water) | | 0,2±0,1 | 1,2±0,1 | 3,5±0,1 | 32±4,0 | 0,2±0,05 | 0,03±0,01 |

*I - before enrichment, II - after enrichment

Note: Commas indicate decimal points.

TABLE 39.* HYGIENIC EVALUATION OF WATER REGENERATED BY THE MEMBRANE METHOD FROM A CONDENSATE OF ATMOSPHERIC MOISTURE (M ± m)

| Parameters | Cellophane | | | Film 100 | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | p, % | 1 | 2 | p, % |
| Permanganate oxidizability, mg $O_2$/liter | 35±2,0 | 27,8±2,82 | 9,8 | 160±5,0 | 24,4±0,87 | 3,5 |
| Ammonium nitrate, mg/l | 50±3,0 | 34±0,49 | 6,6 | 70±6,0 | 8,75±0,8 | 9,7 |
| Nitrogen from nitrites | 0,0075±0,002 | 0,0045±0,004 | 7,8 | 0,337±0,12 | 0,0019±0,002 | 9,5 |
| Nitrogen from nitrates | 8,45±1,4 | 0,036±0,002 | 8,9 | — | 0,02±0,0019 | 9,5 |
| Phosphates | 0,035±0,01 | 0,02±0,0019 | 9,5 | 1,7±0,5 | 0,026±0,002 | 7,7 |

Note: 1, Before; 2, After regeneration.

*Note: Commas indicate decimal points.

From the data in the table it also follows that the best hygienic parameters are found in water at a condenser temperature of 5°, but a subsequent increase in the temperature by 15 to 20° caused an increase in the amount of ammonia in the water from 0 to 14 mg/liter at a constant boiling temperature. /202

Hence, on the basis of an analysis of these data it is clear that the best hygienic parameters are associated with water regenerated from urine at temperatures on the order of 30-40° in the evaporator and 5° in the condenser, making it possible so far to consider this temperature range to be optimal for this process.

Regeneration of water from urine by vacuum distillation, as well as by other methods (lyophilization, electrodialysis) makes it possible to free water of most impurities, without making it conform to the conditions of the All-Union State Standard.

It must be taken into account in this respect that due to the existence of a comparatively large amount of residual impurities in the water regenerated by the vacuum distillation method in comparison with other methods, the development of a unit for further purification acquires particular significance in this case. Hence, it made sense to deal with problems of further purification of regenerated water in this section. In order to bring the quality of the water up to the necessary sanitary and hygienic standards, it was necessary to develop a system for purifying it further with respect to both inorganic and organic impurities. Elimination of ammonia and a number of other organic compounds was accomplished by means of highly acid cationite (KU-2) (subsequently KU-2-8 and KU-2-16), while activated charcoal (AG-5) was used to extract the organic impurities. It was found that AG-5 charcoal has higher

sorptive properties with respect to organic impurities in the liquid phase than does BAU, SKT or other types of charcoal. It was shown that the most effective process for further purification is achieved in sorption columns 10 mm in diameter and 300 mm tall with liquid throughput of 100 ml/hour. The weight of the sorbents with which such a column was charged was 12 g. The sanitary and hygienic studies of water that had passed through sorbents to determine its content of organic impurities, ammonia, nitrates, nitrites, and other components was used to determine the minimum amount of sorbents that would ensure the maximum purification of water with respect to impurities. On the basis of sanitary and hygienic studies it was found that in order to purify one liter of regenerated water it is necessary to have 1.2 g of KU-2 cationite and 3.3 g of AG-5 activated charcoal.

The technological parameters set forth above, required for additonal purification of water regenerated from urine by the vacuum distillation method, also made it possible to use this process for water recovered by the catalytic and lyophilic methods. Hence, as a result of these studies, it was considered possible to perform the regeneration process using urine to obtain water by the vacuum distillation method with minimum energy consumption and at an appropriate vacuum. /203

At the end of these experiments, an experimental regeneration system of metal was designed and built. Water regenerated from urine in this device was not only subjected to exhaustive hygienic evaluation but was also given comprehensive toxicological testing in animals and in appropriate experiments on human beings.

Hygienic Evaluation of Water Regenerated By The Oxidation-Catalytic Method

The basic principles of the oxidation-catalytic method of water regeneration from urine and other moisture-containing waste products, as well as the technological parameters of the operation of the device, have been discussed in the corresponding section.

In the following we shall deal with a number of experiments that have been performed for the purpose of optimization of the processes of water regeneration from urine by the oxidation-catalytic method. It is natural that we should be primarily interested in this regard in the hygienic parameters of the quality of water which is obtained from regeneration systems using various technological operating modes. In our opinion, it is advantageous to present some data which characterize the quality of the regenerated product, for example as a function of the catalyst used, its temperature, depth of the layer, etc. Table 43 shows some of the data that characterize the quality of water regenerated from urine using various catalysts. In all of the experiments, the temperature of the catalytic furnace was 150°, the consumption of the vapor-gas-air mixture was 4.0 liters/minute, the urine evaporation temperature was 100° and the condensation temperature was 15-20°.

TABLE 40.* SANITARY AND HYGIENIC PARAMETERS OF THE QUALITY OF WATER REGENERATED FROM URINE BY THE LYOPHILIZATION METHOD

| Temperature conditions, degrees C | Urine, ml | Amount of water obtained, ml | Dry residue, g | Time of experiment, hours | Yield, ml/hour | pH | Oxidizability (permanganate), mg $O_2$/l | Oxidizability (bichromate), mg $O_2$/l | Nitrogen ($NH_3$), mg/l | Nitrogen from nitrites, mg/l | Nitrogen from nitrates, mg/l | Chlorides, mg/l | Phosphates, mg/l | Total hardness, mg·eq/l | Calcium, mg·eq/l | Magnesium, mg·eq/l | Potassium, mg/l | Sodium, mg/l | Transparency, cm | Chromaticity, degrees | Odor, degrees | Cloudiness, cm | Suspended materials, mg/l | Urea, mg/l | Uric acid, mg/l | Creatine, mg/l | Number of microbes, microbes/ml |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Evaporator, —20——30* | 150 | 143 | 7,1 | 17 | 8,5 | 6,5 | 17,1 | — | 13,4 | 0,06 | — | 60 | 0,25 | 0 | 0 | 0 | 0 | 0 | 25 | 10 | 2 | 0 | 0 | 0 | 0 | 0 | 3600 |
| Condenser, —70——78 | 150 | 144 | 6,3 | 17 | 8,5 | 6,0 | 23,8 | — | 14,4 | 0,02 | — | 30 | 0,11 | 0 | 0 | 0 | 0 | 0 | 25 | 10 | 2 | 0 | 0 | 0 | 0 | 0 | 1200 |
| Evaporator, —10——15* | 300 | 286 | 14,2 | 5,5 | 52,3 | 6,0 | 28,8 | — | 3,5 | 0,02 | 0,17 | 60 | 0,01 | 0 | 0 | 0 | 0 | 0 | 20 | 10 | 3 | 0 | 0 | 9,5 | 2 | 0 | |
| Condenser, —70——78 | 300 | 287 | 13,6 | 5 | 57,1 | 6,0 | 19,2 | — | 4,0 | 0,01 | 0,22 | 42 | 0,08 | 0 | 0 | 0 | 0 | 0 | 20 | 10 | 3 | 3 | 0 | 3,0 | 0 | 0 | |
| Evaporator, —5——7 ** | 300 | 287 | 13,9 | 5 | 57,4 | 6,0 | 19,6 | — | 4,2 | 0,01 | — | 38 | 0,08 | 0 | 0 | 0 | 0 | 0 | 20 | 10 | 3 | 0 | 0 | 0 | 0 | 0 | |
| Condenser, —70——78 | 300 | 286 | 14,8 | 5 | 57,4 | 6,5 | 18,8 | — | 4,3 | 0,02 | — | 40 | 0,08 | 0 | 0 | 0 | 0 | 0 | 20 | 10 | 3 | 0 | 0 | 0 | 0 | 0 | |
| Evaporator, —10—15 ** | 300 | 286 | 14,2 | 5 | 57 | 6,0 | 18,1 | — | 2,6 | 0,01 | — | 35 | 0,03 | 0 | 0 | 0 | 0 | 0 | 20 | 10 | 3 | 0 | 0 | 0 | 0 | 0 | 50 |
| Condensor, —30——40 | 300 | 285 | 15,6 | 5 | 57 | 6,0 | 14,4 | — | 3,5 | 0,01 | — | 10 | 0,05 | 0 | 0 | 0 | 0 | | 20 | 10 | 2 | 0 | 0 | 0 | 0 | 0 | — |
| Evaporator, —5—10 ** | 300 | 285 | 15,4 | 2 | 142 | 6,5 | 20,6 | — | 1,7 | 0,02 | 0,12 | 52 | 0,03 | 0 | 0 | 0 | 0 | 0 | 25 | 10 | 2 | 0 | 0 | 0 | 0 | 0 | 2 |
| Condenser, —25——30 | 300 | 285 | 15,7 | 2 | 142 | 6,5 | 23,4 | — | 3,5 | 0,02 | 0,12 | 60 | 0,27 | 0 | 0 | 0 | 0 | 0 | 25 | 10 | 2 | 0 | 0 | 0 | 0 | 0 | — |
| Evaporator, —10—+15 | 500 | 478 | 23,1 | 4 | 119 | 6,0 | 3,0 | 15,3 | 0,5 | 0,01 | 0,12 | 3,7 | 0,02 | Сл. | Сл. | Сл. | — | — | 25 | 12 | 2 | 0 | 0 | 0 | 0 | 0 | — |
| Condenser, —10——15 | 500 | 479 | 20,9 | 4 | 119 | 6,0 | 1,6 | 10,2 | 1,5 | 0,01 | 0,12 | 3,9 | 0,02 | | | | — | — | 25 | 12 | 2 | 0 | 0 | 0 | 0 | 0 | — |
| Evaporator, —10—+15 | 500 | 425 | 75 | 3 | 141 | 6,0 | 3,5 | 8,9 | 1,2 | 0,03 | 0,12 | 5,7 | 0,02 | Сл. | Сл. | Сл. | — | — | 25 | 12 | 0 | 0 | 0 | 0 | 0 | 0 | — |
| Condenser, —10——15 | 500 | 425 | 130 | 3 | 130 | 6,0 | 5,3 | 16 | 0,6 | 0,01 | 0,17 | 5,2 | 0,02 | | | | — | — | 25 | 12 | 0 | 0 | 0 | 0 | 0 | 0 | — |

*With preliminary freezing of the product. **Self-freezing and heating of the produ t.

*Note: Commas indicate decimal points.

TABLE 41.* HYGIENIC EVALUATION OF WATER REGENERATED FROM 500 ml OF URINE USING THE LYOPHILIZATION METHOD IN REPEATED EXPERIMENTS WITHOUT REMOVAL OF THE DRY RESIDUE

| Parameters | Time, in days | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| Amount of water obtained, ml | 476 | 478 | 475 | 481 | 475 | 476 | 475 | 475 | 475 | 475 | 475 |
| Amount of dry residue, g | 24,8 | 22,8 | 25,2 | 19,6 | 25,1 | 24,2 | 25,3 | 25,0 | 24,8 | 24,8 | 25,2 |
| pH | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
| Permanganate oxidizability | 4,0 | 4,6 | 4,5 | 4,0 | 3,6 | 4,0 | 2,0 | 2,0 | 2,2 | 2,5 | 2,3 |
| Bichromate oxidizability | 12,8 | 15,3 | 14,0 | 14,0 | 12,8 | 14,0 | 12,0 | 12,8 | 14,0 | 11,5 | 14,0 |
| Nitrogen from ammonia, mg/l | 1,8 | 7,0 | 5,6 | 6,0 | 3,8 | 4,8 | 4,6 | 2,6 | 3,5 | 4,5 | 3,5 |
| Nitrogen of nitrites, mg/l | 0,01 | 0,04 | 0,01 | 0,01 | 0,01 | 0,01 | 0,01 | 0,01 | 0,01 | 0,01 | 0,07 |
| Nitrogen of nitrates, mg/l | 0,1 | 0,1 | 0,2 | 0 | 0 | 0 | 0,02 | 0,05 | 0 | 0,1 | 0 |
| Chlorides, mg/l | 2,4 | 2,1 | 2,8 | 2,4 | 2,6 | 2,4 | 2,8 | 2,8 | 3,5 | 3,5 | 5,6 |
| Phosphates, mg/l | 0,009 | 0,005 | 0,07 | 0,01 | 0,07 | 0,02 | 0,02 | 0,06 | 0 | 0 | 0 |
| Sulfates, mg/l | 9,6 | 10,0 | 9,6 | 9,6 | 10,0 | 10,5 | 10,5 | 11,5 | 11,5 | 12,9 | 12,9 |
| Total hardness, mg·eq/l | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Calcium, mg·eq/l | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Magnesium, mg/l | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Potassium, mg/l | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Sodium, mg/l | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Transparency, cm | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 |
| Chromaticity, degrees | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Odor, degrees | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Duration of experiment, hours | 3 | 3 | 3 | 3 | 4 | 5 | 4 | 4 | 5 | 5 | 5 |
| Yield, ml/hour | 159 | 159,3 | 155,3 | 160 | 124 | 95 | 124 | 124 | 95 | 95 | 95 |

*Note: Commas indicate decimal points.

These studies of the regenerated water show that it is most effectively purified by using hopcalite, palladium, and the oxides of chromium and nickel as catalysts. In view of the possibility of nickel and chromium entering the drinking water in large quantities, which may not be indifferent to the health of a living organism, we recommended hopcalite as the catalyst.

The second important question that arises in the development of regeneration systems is that of the influence of the catalyst temperature on the quality of the water regenerated from urine. Studies were performed using laboratory devices in which the hopcalite charge was 100 grams and the other parameters of the experiment corresponded to those set forth above.

TABLE 42.* /RELATIONSHIP BETWEEN THE CHEMICAL COMPOSITION OF WATER REGENERATED FROM URINE BY THE VACUUM DISTILLATION METHOD AND THE TEMPERATURE CONDITIONS OF EVAPORATION AND CONDENSATION

| Temperature, °C | | amount | | Time of experiment, hours | pH | Oxidizability, mg $O_2$/liter | | Nitrogen, mg/l | | | Chlorides, mg/l | Sulfates, mg/l | Phosphates, mg/l | Total hardness, mg·eq/l | Ca, Mg, mg/l |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Evaporation | Condensation | Urine | Regenerated water | | | Permanganate | Bichromate | $NH_3$ | $NO_2^-$ | $NO_3^-$ | | | | | |
| 20 | 5 | 300 | 250 | 4,0 | 8,5 | 20,0 | — | 13,0 | 0,10 | 0,04 | 6,40 | — | — | traces | traces |
| | | 200 | 175 | 6,0 | 8,0 | 16,0 | 24 | 20,0 | 0,02 | 0,12 | 22,0 | — | — | traces | traces |
| | | 500 | 435 | 6,0 | — | — | — | — | — | — | — | — | — | — | — |
| 30 | 5 | 500 | 435 | 5,5 | 5,5 | 4,50 | — | 0,0 | 0,40 | 0,00 | 5,00 | 14,4 | 0,04 | 0 | 0 |
| | | 500 | 475 | 6,0 | 5,5 | 2,60 | 13 | 0,1 | 0,20 | 0,12 | 5,00 | 9,0 | 0,02 | 0 | 0 |
| | | 500 | 480 | 5,5 | 5,5 | 2,40 | 13 | 0,2 | 0,40 | 0,38 | 5,10 | 13,4 | 0,02 | 0 | 0 |
| 30 | 10 | 500 | 430 | 5,5 | 5,5 | 2,40 | 13,0 | 0,2 | 0,41 | 0,40 | 5,10 | 13,4 | 0,02 | 0 | 0 |
| | | 500 | 455 | 7,5 | 5,5 | 1,70 | 13,0 | 0,4 | 0,07 | 0,20 | 6,00 | 2,4 | 0,00 | traces | traces |
| | | 500 | 480 | 7,5 | 5,5 | 4,10 | 8,0 | 0,4 | 0,28 | 0,20 | 7,10 | 2,4 | 0,01 | traces | traces |
| 30 | 15 | 500 | 475 | 6,5 | 5,5 | 2,30 | 80 | 0,4 | — | — | — | — | — | — | — |
| | | 500 | 450 | 5,5 | 6,0 | 1,60 | 37,3 | 1,6 | 0,02 | 0,50 | traces | — | 0,02 | 0,36 | 12,5 |
| | | 500 | 430 | 5,0 | — | 1,00 | — | 1,9 | — | — | — | — | — | — | — |
| 30 | 20 | 500 | 480 | 5,5 | 6,0 | 1,10 | 73,6 | 14,3 | 0,03 | — | 2,80 | — | — | — | traces |
| | | 500 | 450 | 5,0 | 6,0 | 1,50 | 96 | 15,0 | — | — | 8,50 | — | 0,04 | — | traces |
| | | 500 | 435 | 5,5 | 6,0 | 1,40 | 40 | 12,4 | — | — | — | — | 0,02 | — | — |
| 50 | 5 | 500 | 450 | 4,5 | 7,5 | 4,50 | 40 | 8,5 | 0,00 | — | 8,50 | 2,8 | 0,01 | — | 2 |
| | | 500 | 435 | 4,0 | 6,0 | 33 | 96 | 40 | 0,02 | 0,48 | 5,70 | 2,6 | — | — | — |
| | | 500 | 400 | 4,0 | 7,5 | 147 | 373 | 42 | 0,02 | 0,50 | 9,30 | 3,9 | 0,02 | — | — |

*Note: Commas indicate decimal points.

TABLE 43.* QUALITATIVE COMPOSITION OF WATER REGENERATED FROM URINE BY THE OXIDATION-CATALYTIC METHOD

| Type of catalyst | pH | Oxidizability, mg $O_2$/liter | Total hardness, mg·eq/liter | Nitrogen, mg/liter | | | | | | | Odor, points | Transparency, cm | Chromaticity, Degrees |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $NH_3$ | $NO_2^-$ | $NO_3^-$ | Urea | Uric acid | Creatinine | Total | | | |
| Traces | 7,0±1,0 | 4,0±1,0 | 0 | 7,1±0,3 | 0,07±0,01 | — | 0 | 0 | 0 | 7,3±1,1 | 0 | 30 | 5 |
| Hopcalite, Activated charcoal with catalytic additive, oxides: | 7,2±1,0 | 2,0±0,5 | Следы | 40,0±5 | 0,02±0,3 | 0,1±0,05 | 0 | 0 | 0 | 41,0±2,7 | 1 | 30 | 5 |
| Chromium | 6,0±1,2 | 0,8±0,3 | 0 | 11,0±2,0 | 0,09±0,01 | 0,4±0,1 | 0 | 0 | 0 | 12,0±1,2 | 0 | 30 | 5 |
| Nickel | 6,0±1,0 | 1,0±0,5 | 0 | 10,0±1,0 | 0,09±0,005 | 0,0 | 0 | 0 | 0 | 11,0±1,0 | 0 | 30 | 10 |
| Iron | 9,0±1,0 | 7,0±1,0 | 0 | 180±10 | 0,01±0,003 | 5,6±0,9 | 0 | 0 | 0 | 186,0±12 | 3 | 30 | 10 |
| SBS-4 ionite | 9,0±1,0 | 51,0±3,0 | 0 | 116,0±12 | 0,70±0,1 | 23,0±2,0 | Следы | Следы | 0 | 140,0±8 | 5 | 30 | 10 |
| Platinum | 6,0±1,2 | 1,4±0,5 | 0 | 33,0±6 | 0,23±0,08 | 11,0±1,0 | 0 | 0 | 0 | 44,5±2,4 | | 30 | 5 |
| Palladium | 6,0±1,3 | 6,7±0,9 | 0 | 11,9±2 | 0,90±0,09 | 10,2±1,7 | 0 | 0 | 0 | 23,6±19 | | 30 | 5 |
| AK-62 | 9,0±0,5 | 1,6±0,4 | Сл. | 157,0±13 | 3,20±0,1 | 13,1±1,2 | 0 | 0 | 0 | 170,5±13 | | 30 | 10 |

TABLE 44.* SANITARY-HYGIENIC PROPERTIES OF WATER REGENERATED FROM URINE WITH VARIOUS CATALYST TEMPERATURES

| Temperature of catalyst (in °C) | pH | Oxidizability, mg $O_2$/liter | Nitrogen, mg/liter* | | | | Total hardness, mg·eq/liter | Chlorides, mg/liter | Odor | Transparency, cm | Chromoticity, points |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $NH_3$ | $NO_2^-$ | $NO_3^-$ | Total | | | | | |
| 70 | 8,0±1,0 | 26,5±1,2 | 75,0±5 | 0,08±0,09 | 36±3,0 | 111,8±10 | Traces | 43,6±4 | Strong (Urine) | 30 | 10 |
| 80 | 7,6±0,8 | 25,5±1,3 | 82,0±3 | 1,2±0,05 | 62±5 | 114,6±9 | " | 52,5±6 | Urine | 30 | 10 |
| 100 | 7,5±0,6 | 10,9±0,9 | 57,0±6 | 0,36±0,07 | 24±2 | 81,4±7 | 0 | 39,0±3 | Weak (Urine) | 30 | 5 |
| 120 | 7,6±1,0 | 5,0±1,0 | 60±5 | 0,75±0,1 | 41±6 | 101,8±12 | 0 | 38,3±5 | None | 30 | 5 |
| 130 | 7,6±1,2 | 4,0±0,7 | 58,0±3 | 1,1±0,1 | 46±4 | 105,1±6 | Traces | 41,9±4 | " | 30 | 5 |
| 140 | 7,5±0,9 | 3,2±0,6 | 44,0±1,9 | 0,07±0,02 | 23±3 | 67,1±3 | 0 | 31,2±6 | " | 30 | 5 |
| 150 | 7,6±0,7 | 3,1±0,9 | 50±6 | 0,15±0,09 | 0,25±0,1 | 50,5±2 | 0 | 35,5±3 | " | 30 | 5 |
| 200 | 7,2±1,1 | 3,4±0,5 | 20±3 | 1,5±0,07 | 0,24±0,2 | 45,0±4,0 | 0 | 28,1±4 | " | 30 | 5 |
| 400 | 4,5±0,09 | 14,0±0,9 | 5,0±0,9 | 11,0±3,0 | 0,3±0,09 | 16,5±1,8 | 0 | 3,55±1 | " | 30 | 5 |
| 500 | 2,5±0,7 | 18,0±1,0 | 1,0±0,2 | 13,0±2,0 | 0,39±0,08 | 41,5±1,6 | 0 | 0 | " | 30 | 5 |

*Note: Commas indicate decimal points.

Studies to determine the minimum temperatures of the catalyst which would ensure maximum purification of water are of great practical significance for carrying out the water regeneration process with minimal energy consumption. Table 44 lists the data from sanitary-hygienic evaluations of water regenerated /204
from urine under various temperature conditions in the catalytic furnace. The data in the table indicate that when the catalytic furnace is at 100° or more, a high degree of oxidation of the organic substances contained in the urine results. On one hand, this is supported by the low values of the oxidability /205
of the regenerated product at catalytic furnace temperatures from 100 to 200°. However, when the temperatures are 400-500° the level of oxidability increases. The explanation for this effect is shown in page 85. The completeness of the oxidation of the organic impurities at a catalyst temperature of 100° or more, on the other hand, is supported by the lack of urea and the specific odor of /206
urine in the regenerated water.

Hence, the optimum recommended catalyst temperature was 150°, which ensured mineralization of the organic impurities making up the urine with minimum energy consumption. Impurities that remained in the regenerated product, as a rule, were of inorganic origin and could be completely eliminated by passing the product through appropriate sorbents.

It is also quite interesting to study the influence of urine evaporation temperature on the chemical composition of the regenerated water. The results of these experiments are shown in Table 45. It follows from the data in the table that at an evaporation temperature of 50° the water regenerated from urine contains the smallest amount of impurities and, after appropriate treat- /207
ment, may be recommended for drinking. In designing regeneration systems it is also necessary to be aware of the influence exerted on the quality of the regenerated water by such parameters as the depth of the catalyst layer and its minimal permissible weight to ensure the necessary degree of purification. Determination of this relationship was carried out in a reaction with a cross section of 6.5 $cm^2$ with an air flow rate of 4.0 liters/minute. As a catalyst, we used hopcalite with 1-2 mm grains. The results of the studies are shown in Table 46.

From the data in Table 46 it follows that the minimum weight of catalysts which will ensure the necessary purification of the water regenerated from the urine and will ensure that this water contains the minimum quantity of impurities is 50 grams. In the course of these studies the principal impurity in the regenerated water was found to be ammonia. Hence, it was interesting to determine the ammonia excretion rate as a function of the degree of extraction of water from urine.

It was found that the rate of ammonia formation increases in inverse proportion to the increase in the temperature of the catalytic furnace and in direct proportion to the degree of water extraction.

Studies of water regeneration by the catalytic method from highly concentrated products of vital activity showed the possibility of using this method as a reliable way of reclaiming water for repeated human use. The positive aspect of this method is that it makes it possible to oxidize the stable

organic impurities that are contained in waste products and turn them into simple, readily absorbed chemical compounds such as $CO_2$, $NH_3$, $H_2O$, etc. Hence, by using catalytic methods, it is practically possible to solve completely the problem of eliminating all organic impurities from water by oxidizing them.

TABLE 45.* CHEMICAL COMPOSITION OF REGENERATED WATER VERSUS URINE EVAPORATION TEMPERATURE (°C)

| Parameters | Circulating Device | | | Throughput Device | | |
|---|---|---|---|---|---|---|
| | 50° | 100° | 150° | 50° | 100° | 150° |
| pH | 6,0 | 7,1 | 10,0 | 6,0 | 7,0 | 10,0 |
| Oxidizability, mg $O_2$/liter | 1,5 | 2 | 44,0 | 1,3 | 5,3 | 38 |
| Nitrogen, $NH_3$, mg/l | 1,2 | 40—50 | 1500 | 0,17 | 30—40 | 1300 |
| Nitrogen, $NO_2$, mg/l | 0,02 | 0,03 | 0,05 | 0,015 | 0,01 | 0,04 |
| Nitrogen, $NO_3$, mg/l | 0,12 | 0,7 | 41 | 0,4 | 0,6 | 33 |
| Chlorides, mg/l | — | 50 | 124 | — | 42 | 142 |
| Urea, mg/liter | 0 | 0 | 0 | 0 | 0 | 0 |
| Transparency, cm | 30 | 30 | 30 | 30 | 30 | 30 |
| Chromaticity, degrees | 15 | 15 | 15 | 15 | 15 | 15 |
| Odor, points | 0 | 0 | 5 (ammonia) | 0 | 0 | 5 (ammonia) |

Note: Commas indicate decimal points.

The studies of regenerated water revealed that the most reliable method of reclaiming it from urine is the catalytic method. This view is supported by the data of a one-year experiment in which a regeneration system based on the catalytic method made it possible to recycle water from urine to three subjects during this period of time. /208

Toxicological Study of Water Regenerated by Low-Energy Method from Moisture-Containing Wastes

In the toxicological evaluation of water regenerated by low-energy methods, our most detailed studies involved water that had been regenerated from a condensate of atmospheric moisture and CFC fluid by the sorption method. We know that this method of regeneration of water is considered the most promising one at the present time and is used as the basis of the latest water supply systems for both terrestrial and inflight applications.

The toxicological evaluation of the regenerated water using animals, with subsequent evaluation with human subjects, was carried out with a consideration of further enrichment of the regenerated water, with trace and macroelements. The most complete toxicological study involved water obtained from the condensate of atmospheric moisture.

Acute, subacute and chronic experiments were performed on animals to carry out the toxicological evaluation of the water.

TABLE 46.* INFLUENCE OF WEIGHT AND LAYER THICKNESS OF CATALYSTS ON CHEMICAL COMPOSITION OF REGENERATED WATER

| Weight, grams | Thickness, mm | pH | Oxidizability, $O_2$ mg/liter | Nitrogen, mg/liter | | Nitrogen, mg/liter | | Total hardness, mg·eq/liter | Odor, points | Transparency, cm | Chromaticity, degrees |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $NH_3$ | $NO_2^-$ | $NO_3^-$ | Total | | | | |
| 20 | 35 | 8,5±0,9 | 13,0±2 | 89,0±10 | 0,20±0,05 | 0,20±0,03 | 190,0±0 | Traces | 3 | 30 | 10 |
| 40 | 75 | 8,2±1,0 | 10,6±1 | 81,0±8 | 0,50±0,07 | 0,10±0,009 | 82,0±8 | Ditto | 3 | 30 | 10 |
| 50 | 90 | 8,0±1,1 | 3,0±0,8 | 36,0±3 | 0,25±0,03 | 0,08±0,01 | 38,0±4 | " " | 0 | 30 | 5 |
| 80 | 145 | 7,0±1,3 | 3,4±0,6 | 35,0±4 | 0,60±0,04 | 0,29±0,07 | 36,0±5 | 0 | 0 | 30 | 5 |
| 100 | 180 | 7,2±0,9 | 3,6±0,4 | 40,0±5 | 0,60±0,05 | 0,02±0,008 | 41,0±3 | 0 | 0 | 30 | 5 |

*Note: Commas indicate decimal points.

In view of the considerable diversity of the impurities that go to make up the original products used for water regeneration, selection of methods for toxicological evaluation emphasized tests which would allow evaluation of the degree of total toxicity. For this purpose, we performed tests in an acute experiment on daphnia (Daphnia rubra) and the isolated frog heart using generally accepted methods (Drachev, 1956; Kravskov, 1911). We know that these methods are sensitive indicators that can be used in evaluating the degree of water purification (Bazarova, 1930). In a subacute experiment, we studied the local and general effects of enriched regenerated water obtained by the sorption method on the organism of the rabbit for a period of one month. For this purpose, the water under study was placed in the conjunctival sac of the animal and was also injected subcutaneously. This method is widely used in toxicological studies (Moiseyev, 1952; Pravdin, 1960). In a chronic experiment, we studied the prolonged influence of enriched regenerated water on the organism of the white rat when administered orally for six months. Experiments were performed on 120 animals with an initial weight of 140-170 grams, 20 animals per group. The control animals obtained enriched distilled or tap water. In addition to regular observation of the external appearance, growth and weight of the animals and the amount of water which they used, we studied /209 the following physiological parameters:

a) total blood analysis, including a determination of the number of leucocytes, neutrophils with segmented nuclei, lymphocytes, monocytes, eosinophils and reticulocytes;
b) the osmotic resistance of the erythrocytes;
c) the phagocytic activity of the leucocytes;
d) activity of thymol (SH)-groups of blood serum;
e) the antitoxic function of the liver (test with hexanal anesthesia);
f) enzymatic activity of potassium alkaline phosphatase.

We also performed a pathohistological study of a number of internal organs. The physiological parameters were recorded prior to the experiment (background), and 1, 1.5, 2, 4 and 6 months following the start of the experiment.

Studying a number of hematological parameters, including the phagocytic activity of leucocytes, allows a detailed determination of the condition of the total reactivity of the organism and its immunobiological properties (Kozlova, 1960; Velling, 1959). All of the blood parameters were studied using generally accepted methods (Predtechenskiy, 1950; Volkova, 1965). It was found that the study of the osmotic resistance of the erythrocytes reflects the condition of the general resistance of the organism and its adaptation to the effects of environmental factors. An increase in the resistance of the organism is accompanied by an increase in the osmotic resistance of the erythrocytes, while a decrease on the other hand is indicative of exhaustion of the organism and a decrease in its adaptational capacity. The parameters of osmotic resistance were studied using an appropriate method (Barbashova, 1963).

A decrease in the activity of the thymol (SH)- groups in the blood serum serves as a sensitive indicator of the chronic intoxication of the organism

(Azyavchik, 1954). The determination of the sulfhydryl groups was carried out using the method of amperometric titration (Kedrova, 1962). In view of the fact that water taken internally comes in contact primarily with the mucuous membranes of the gastrointestinal tract, where its toxic action may occur, we studied potassium alkaline phosphatase as one of the indicators of the enzymatic activity of the intestine (Fomina, 1964).

We know that any toxic effect on the organism is bound to be reflected primarily in the detoxifying function of the liver. For this purpose, determining the period of hexanal anesthesia of the animals was conducted using an appropriate method (Broytman, 1966). In order to detect morphological changes in the organs and tissues of the animals that were associated with the experiment, these organs were subjected to a pathohistological examination. The experimental data obtained from these toxicological studies were statistically analyzed using the Student method.

In conclusion, the sorption method of regeneration of water, tested on animals, was approved in tests which involved the use of water regenerated from a condensate for 2-12 months. An analysis of the data in the literature also indicates that the method of study which we employed ensured that the regenerated water was hygienically evaluated from all aspects and that we were subsequently able to recommend its use for drinking aboard spacecraft (Cherkinskiy, 1964; Yelizarova, 1962). It was also necessary to study the influence of enriched regenerated water on the living organism. /210

Influence of Water Regenerated by the Sorption Method from a Condensate of Atmospheric Moisture on the Organisms of Animals and Man

We know that a final evaluation of the degree of detoxification of water for the organism can only be done on the basis of a thorough analysis of data from acute, subacute and chronic animal experiments. The study of the influence of enriched regenerated water from sorption devices on the organism in an acute experiment failed to produce consistent results. Thus, in experiments with daphnia, we found no unfavorable effects on the animals that were produced by the water under study in comparison with controls. At the same time, however, there was a shortening of the time of activity of the isolated frog heart in water regenerated by the sorption method. However, studies in a subacute experiment failed to confirm any symptoms of the toxic action of enriched regenerated water that were associated with local or general effects on animals. We were particularly interested in studying the influence of enriched regenerated water on animals under conditions of prolonged usage.

Observation of animals in a chronic experiment showed that under the influence of six months' drinking of enriched regenerated water there was no negative influence of any kind on the general condition, weight dynamics or physiological parameters (Tables 47-49). An analysis of the data obtained indicates the practical nonexistence of any toxic effects of enriched water on the organism when this water was regenerated from the condensate of atmospheric moisture. However, there were slight deviations in the dynamics of certain hematological parameters, osmotic resistance of erythrocytes and weight of rats during the period of their intensive growth in a group of

animals that obtained water from the regeneration system. These changes, however, were not reliable and as a rule did not go beyond the limits of corresponding physiological norms. They may be explained by an adaptation of the organism to the new environmental factor, in this case water, which is supported by similar examples under natural conditions. The lack of a general toxic effect of the water on the animals is also supported by a study of other physiological parameters and pathomorphological studies of organs and tissues /213 at the end of 2, 4 and 6 months of experimentation. The results we obtained from our toxicological study of animals that used regenerated enriched water indicated that there was a possibility of performing further experiments involving human participation. For this purpose, in experiments involving various periods of exposure, as well as a long one-year experiment, the water which the subjects used for drinking and for preparing their meals was regenerated from a condensate by the sorption method and enriched with mineral components using a method which we have devised. An analysis of the special questionnaires filled out by the subjects indicated that they had no significant complaints regarding their state of health or the quality of the water which they used. This is supported by the data from a systematically performed chemical analysis of the water, indicating that its sanitary and hygienic properties were very good. From data collected in clinical-physiological observations in the course of a careful monitoring of the subjects' health, it was also found that the water which they used was completely adequate and failed to cause any problems affecting their organisms. Isolated changes that did occur were temporary and constituted reactions characteristic of the exposure of human beings to hermetically sealed volumes. All of this indicates that water regenerated from the products of human vital activity and enriched with a number of mineral components and trace elements does not have a negative influence on the human organism and promotes the normal course of functioning of the organism when used for long periods of time.

Special emphasis should be placed on hygienic and toxicological studies of water regenerated by the sorption system from moisture given off by fuel cells (electrochemical generators).

Studies of Water Regenerated from the Condensate of the Fuel Cells with the Potassium Electrolyte Method of Sorption Purification

The toxicological evaluation of the condensate of fuel cells, working with potassium electrolyte purified on resins, KU-2 $(H)^+$ and AV-17 $(SiF_6)$, was performed on 30 male white rats for two months. At the same time, 10 control animals were given water from the Moscow city water supply. All three groups were kept in cages during the experiment and were fed a basic diet without using milk as a detoxifying product. To evaluate the influence of the water under study, containing ionic silver at a concentration of 0.8 mg/liter as a preservative and passed through KU-2 and AV-17 resins as well as being enriched with appropriate minerals, the following tests were performed:

- observation of the external appearance, behavior and increase in weight of the experimental and control animals;
- determination of the number of the leucocytes in the blood; /214

- determination of the osmotic resistance of the erythrocytes;
- determination of the number of free sulfhydryl groups in the blood serum;
- study of the antitoxic function of the liver (test with hexanal);
- determination of the activity of adenosine triphosphatase in the brain and liver of experimental and control animals. During the entire experiment, all three groups of animals were maintained under the same conditions. However, the external appearance of the rats that were given water to drink that had been purified with AV-17 was still worse at the end of the first month of drinking and prior to the end of the experiment than in the case of the others: the fur was less smooth, the animals were inactive, drank their water less willingly, and the cutaneous coverings around the nose were inflamed and covered with encrustations. During the second month of drinking this water, a pronounced transverse striation appeared on the upper and lower incisors -- characteristic symptoms of fluorosis. Two rats in this group died. When the other two rats were autopsied, they were both found to be suffering from acute suppurative otitis and frontitis. The animals in this group, by the end of the second month of drinking the water, showed a slightly reduced weight gain in comparison with the others, and after two and a half months of drinking the water the weight loss was 3-4 grams on the average in comparison with two months of drinking.

When the number of leucocytes in the peripheral blood of these animals was analyzed, we were struck by the increase in their numbers in the control group at the end of the first month of drinking, and in the experimental animals by the end of the second month of the experiment. This physiological change, linked to the time of year, was clearly evident in the control animals and markedly inhibited in the experimental groups:

| Method of Purification of Water | Number of Leucocytes, Thousands | | |
|---|---|---|---|
| | Background | 1 month | 2 months |
| AV-17 ($SiF_6$) + $Ag^+$ | 11.2 | 11.7 | 16.0 |
| KU-2 + $Ag^+$ | 11.7 | 12.7 | 15.2 |
| Control | 14.2 | 19.7 | 21.4 |

An analysis of the data on the study of the osmotic resistance of the erythrocytes failed to reveal any important differences between the experimental and control animals. The number of free SH-groups in the blood serum of the experimental and control animals who drank the experimental water that had been purified with KU-2 resin remained practically at the same level during the entire experiment, while in the group of rats that drank water purified with AV-17 ($SiF_6$) the number of SH-groups had increased after two months of drinking. This increase in the SH-group content in the blood serum was statistically reliable not only in the controls but during the first month of drinking.

TABLE 47.* CHANGE IN CERTAIN PHYSIOLOGICAL PARAMETERS IN ANIMALS USING REGENERATED WATER FOR TWO AND SIX MONTHS (M ± m)

| Water | Weight | | | Phagocytic Activity of Leucocytes, %: | | Phagocytic number, units | | Sulfhydryl groups (mMsh/100 ml of serum) | | Duration of hexanol anesthesia, minutes | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Background | 2 | 6 | Background | 6 | Background | 6 | Background | 6 | Background | 6 |
| Tap water | 217±6,0 | 295±9,2 | 496±15 | 5,0±0,9 | 5,3±0,7 | 0,1±0,02 | 0,12±0,01 | 50±3,9 | 54±2 | 36±1 | 36±0,6 |
| distilled water | 215±6,0 | 297±4,9 | 453±4,6 | 6,1±0,8 | 5,8±0,1 | 0,08±0,01 | 0,1±0,02 | 54±2,2 | 57±1,5 | 38±1 | 38±1 |
| regenerated water enriched with salts | | | | | | | | | | | |
| device 1 | 203±3,1 | 269±7,4 | 458±1,0 | 5,1±0,6 | 6,0±0,7 | 0,08±0,02 | 0,09±0,01 | 46±2 | 50±3 | 37±1 | 38±1 |
| device 2 | 205±5,6 | 272±6,1 | 454±9,9 | 7,1±0,5 | 5,3±0,5 | 0,11±0,02 | 0,12±0,02 | 57±5 | 60±2 | 28±1 | 38±0,6 |
| device 3 | 219±9,9 | 259±4,8 | 448±20 | 5,6±1,1 | 5,5±0,8 | 0,06±0,01 | 0,08±0,01 | 56±0,7 | 54±2 | 38±2 | 29±0,38 |

TABLE 48.* CHANGE IN FORMED ELEMENTS OF THE WHITE BLOOD IN EXPERIMENTAL ANIMALS GIVEN REGENERATED WATER TO DRINK FOR SIX MONTHS (M ± m)

| Water | Leucocytes, thousands | | Segmented neuclei, % | | | Lymphocytes, % | | | Monocytes, % | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Background | 6 | Background | 4 | 6 | Background | 4 | 6 | Background | 4 | 6 |
| Tap water | 15,7±1,5 | 14,5±1,5 | 20,9±1,8 | 21,5±2,2 | 23,2±0,6 | 71,5±1,2 | 71,3±2,3 | 66,3±2,7 | 4,1±0,4 | 6,0±0,5 | 10,0±1,5 |
| distilled water | 12,6±0,4 | 15,0±2,1 | 19,3±1,1 | 18,0±1,5 | 28,8±1,9 | 75,7±0,9 | 74,7±1,8 | 67,5±2,4 | 3,9±0,3 | 7,3±0,3 | 11,0±0,5 |
| regenerated water enriched with salts | | | | | | | | | | | |
| device 1 | 11,5±1,9 | 14,4±0,9 | 21,0±1,0 | 22,5±3,4 | 32,5±6,1 | 75,8±2,1 | 74,1±1,9 | 66,5±2,3 | 3,0±0,5 | 7,1±1,9 | 9,3±2,3 |
| device 2 | 12,4±1,8 | 14,1±1,7 | 21,6±3,2 | 21,3±1,8 | 35,0±1,5 | 72,5±1,8 | 70,2±1,6 | 63,9±2,9 | 4,7±0,4 | 5,8±0,7 | 6,6±0,6 |
| device 3 | 14,1±0,4 | 18,8±3,1 | 17,5±0,9 | 19,2±1,5 | 37,0±4,7 | 75,5±0,9 | 65,3±3,1 | 53,6±1,5 | 3,7±0,2 | 3,6±0,3 | 6,7±0,7 |

*Note: Commas indicate decimal points.

TABLE 49.* /CHANGES IN SEVERAL HEMATOLOGICAL PARAMETERS IN EXPERIMENTAL ANIMALS AFTER SIX MONTHS' DRINKING REGENERATED WATER (M ± m)

| Water | Eosynophils | | Reticulocytes, units | | | Osmotic Resistance of Erythrocytes, | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Background | 6 | Background | 4 | 6 | P-p NaCl, % | Background | 2 | 6 |
| Tap water | 3,8±0,8 | 3,5±0,2 | 20,3±2,0 | 18,2±2,4 | 38,0±4,9 | 0,42 | 5,5±0,7 | 1,2±0,2 | 4,8±0,8 |
| distilled water | 4,0±1,0 | 3,8±0,2 | 15,3±1,5 | 21,7±3,4 | 52,2±18,2 | 0,50 | 35±0,4 | | 30±0,3 |
| | | | | | | 0,58 | 78±6 | 56±6 | 76±7 |
| regenerated, enriched with salts | | | | | | | | | |
| Device 1 | 1,7±0,4 | 2,4±1,1 | 25,0±1,5 | 24,2±1,0 | 46,7±6,4 | 0,42 | 6,1±1,0 | 2,6±0,4 | 7,9±1,0 |
| | | | | | | 0,50 | 49±3 | 27±2 | 44±3 |
| | | | | | | 0,58 | 89±4 | 57±4 | 93±6 |
| Device 2 | 2,6±1,0 | 2,3±0,2 | 21,4±1,8 | 15,7±2,5 | 26,0±5,2 | 0,42 | 8,1±2 | 5,4±0,4 | 6,7±2 |
| | | | | | | 0,50 | 47±5 | 22±3 | 54±5 |
| | | | | | | 0,58 | 87±7 | 48±5 | 90±9 |
| Device 3 | 3,9±0,2 | 2,8±0,7 | 24,7±1,0 | 15,5±0,9 | 29,4±6,4 | 0,42 | 8,4±0,6 | 1,4±0,4 | 13,0±1 |
| | | | | | | 0,50 | 45±3 | 22±2 | 58±3 |
| | | | | | | 0,58 | 64±5 | 52±3 | 90±12 |

*Note: Commas indicate decimal points.

In the following, we have listed the numbers of free SH groups per 100 ml of blood serum in the rats: /215

| Method of Purification of Water | 1 month | 2 months |
|---|---|---|
| AV-17 ($SiF_6$) + $Ag^+$ | 57.6 ± 0.98 | 73.3 ± 2.66 |
| KU-2 + $Ag^+$ | 61.0 ± 3.41 | 60 ± 2.83 |
| Control | 56.0 ± 3.86 | 61.6 ± 0.98 |

When tests were performed with hexanal, we observed a lengthening of the duration of anesthesia in animals that had been drinking water from the fuel cells which had been purified with AV-17 resin ($SiF_6$); the increase in anesthesia was statistically reliable toward the end of the second month of drinking ($t = 3.2$). The decrease in the duration of hexanal anesthesia by the end of the second month of the experiment in the group of animals that drank the experimental water purified with KU-2 resin was statistically unreliable and can evidently be explained by the influence of ionic silver which catalyzes the hydrolysis of molecules of hexanal that takes place in the liver (Algeri McVey, 1956). In the control group of animals, after two months of observation, there were no reliable changes in the rate at which hexanal was broken down by the liver.

The duration of hexanal anesthesia (in minutes) in those animals that received regenerated water was as follows:

| Method of Purification of Water | Background | 1 month | 2 months |
|---|---|---|---|
| AV-17 ($SiF_6$) + $Ag^+$ | 31.3 ± 1.835 | 38.3 ± 5.4 | 37.6 ± 0.330 |
| KU-2 + $Ag^+$ | 31.3 ± 1.835 | 26.3 ± 2.83 | 27.25± 2.49 |
| Control | 31.3 ± 1.835 | 23.3 ± 2.91 | 34.0 ± 1.67 |

The activity of adenosine triphosphatase in the tissues, of the brain and liver during the experiment in those animals that were in the control group and the group that drank water purified with KU-2 resin remained practically the same. A slight increase in the ATP-ase activity in the tissues of the animals by the end of the first month of drinking water purified with AV-17 resin ($SiF_6$) was observed by the end of the second month of drinking. The level of ATP-ase activity returned practically to the original levels:

| Method of Water Regeneration | Brain | | | Liver | | |
|---|---|---|---|---|---|---|
| | Background | 1 month | 2 months | Background | 1 month | 2 months |
| AV-17 ($SiF_6$) + + $Ag^+$ | 13.25 | 14.5 | 13.6 | 14.9 | 18.1 | 15.0 |
| KU-2 + $Ag^+$ | 13.25 | 13.0 | 13.5 | 14.9 | 15.3 | 14.0 |
| Control | 13.25 | 13.5 | 13.1 | 14.9 | 15.6 | 14.0 |

Hence, on the basis of the data obtained from a toxicological study of water regenerated from CFC fluid we can conclude that purifying it with KU-2 ($H^+$) resin failed to have any negative influence on the organism in the course of two months' drinking. However, the use of AV-17 ($SiF_6$) resin for regeneration of water caused a number of changes in the organisms of animals that drank this water. These problems took the form of a deterioration of the general condition of the animals, stabilization of the weight, symptoms of fluorosis and changes in the dynamics of a number of physiological parameters. These conclusions were also supported by data from a physical-chemical analysis of the water which revealed in this case that it had a high fluorine content. /216

The results obtained from this sanitary-hygienic evaluation of water regenerated from the condensate of fuel cells by the sorption method made it possible to issue preliminary medical and biological data which were taken into account in developing water purification technology.

## Toxicological Evaluation of Water Regenerated from Highly Concentrated Moisture-Containing Wastes

We have already discussed the necessity for performing careful tests of water regenerated from products of human vital activity, particularly condensates, involving complex chemical, bacteriological and toxicological studies. However, in selecting methods of hygienic evaluation of water obtained from urine, it was necessary to take into account the specific nature of the raw product; unlike natural water, condensates of atmospheric moisture or fluids from electrochemical generators, this product is characterized by a high content of impurities of both an organic and inorganic nature. We know that urine can contain biologically active substances including steroid hormones, whose entrance into the water is not excluded under certain conditions of water recycling. In this connection, together with the methods of hygienic evaluation of water that are used for low-concentration solutions, it is necessary to remember that a number of additional parameters must be determined in the case of such products as urine. In regenerating water from urine, it was advantageous to provide for its testing to determine the content of a number of biochemical substances including urea, creatinine, steroid hormones, etc. For this purpose, for example, the method of determination of biologically active substances in the urine was used, modified by Krekhova (1960). The basis of the method was the extraction of the steroids by organic solvents (chloroform, ether) with subsequent application of the method of paper chromatography. This method of determination was highly accurate and made it possible to determine the content of the steroids in the water on the order of 2-5 mg/liter. The data obtained show that regenerated water contains practically no corticosteroids (hydrocortisone, aldosterone, corticosterone) or the products of their metabolism (tetrahydro- and dehydro derivatives of these steroids). Hence, it was found that regenerated water does not contain any biologically active substances. Of course, in evaluating water regenerated from urine, a number of methods could be used that would make it possible to evaluate its organic composition, microbial contamination and the influence which it has on the living organism when used for a long period of time. /217

Table 50 presents a comparative listing of the chemical composition of water samples regenerated from urine using the methods of lyophilization, vacuum distillation and catalytic oxidation with subsequent purification using sorbents, taking into account the enrichment of the water with mineral components. Then the water was used for toxicological studies on animals. As we can see from the data in the table, the composition of the water prior to enrichment as a rule resembles that of distilled water and there were practically no impurities of an organic or inorganic nature in it. However, it should be pointed out that in the course of developing technological systems of water purification, residual amounts of certain mineral components were observed in the water which were accompanied by simultaneous increases in the content of products of organic origin in the water. Thus, for example, in some cases the total oxidability of the water obtained from urine by the method of vacuum distillation varied within limits from 1.02 to 15.4 mg $O_2$/liter, and that obtained by catalytic oxidation from 0.32 to 7.7 mg $O_2$/liter, while the lyophilization method gave figures from 0.38 to 7.0 mg $O_2$/liter. In addition, with certain variations in the technological regime, residual hardness in regenerated water on the order of 2.4-4.8 mg·eq/liter was found, mainly due to calcium ions. The content of chlorides, nitrates and phosphates in the water did not exceed the standards set by the All-Union State Standard. Thus, the highest figures for the chlorides were observed when water was distilled from urine -- 274 ± 63 mg/liter; in the case of catalytic oxidation it was on the order of 63 ± 8 mg/liter, and the lowest figures were obtained for lyophilization -- 25 ± 6 mg/liter. These data indicate that in certain methods that require additional purification, for example vacuum distillation of water from urine, the residual amounts of certain components of organic and inorganic in many instances reached significant levels. The preliminary purification of water to achieve this purpose, employing sorbents, led to total demineralization of the water and freed it of organic impurities (see Table 50).

As we can see from the data in the table, following enrichment with mineral components, drinking water was obtained that had high hygienic characteristics that corresponded to all requirements of the All-Union State Standard.

In working out a system for toxicological evaluation of water regenerated from urine and water used for sanitary and hygienic purposes, we employed a number of methods of acute, subacute and chronic experimentation on animals, discussed previously in the section on toxicological evaluation of water from low-concentration products in conjunction with short-term flights. However, due to the more complex chemical composition of urine, toxicological evaluation /219 of water regenerated from it employed more sensitive methods and ones which react rapidly to changes in external conditions, using hydrobionts./

We know that in the toxicology of water, in order to study the influence of the various substances dissolved in water on the living organisms populat-int it, a wide variety of biological methods are employed which do not share a common methodological basis, resulting in considerable difficulty and numerous shortcomings in biological research. In experiments on fish, for example,

aside from the familiar method of the "fish test", methods are employed which demonstrate an increase in living mass, level of intensity of oxygen consumption, etc. In order to establish the toxic effects of various substances under conditions of prolonged action on living organisms, various physiological parameters have been proposed which characterize the status of a number of functional systems in the organism (for example, the cholinesterase activity in the tissues and blood serum and the intensity of erythropoiesis in fish).

A number of authors have indicated essentially two trends in the solution of the problem of the biological criterion of toxicity:

- medical, including veterinary;
- biological, based on the concept of the biological standard.

Corresponding methods of determining the toxicity are distinguished both in terms of the length of the experiment, the selection of the test objects and the selection of the test functions.

In our work, we studied water samples regenerated from human urine by the catalytic method, water samples obtained by the method of catalytic decomposition of hydrogen peroxide and water obtained from fuel cells. Samples of the water to be studied in terms of all of the sanitary-hygienic parameters corresponded to the All-Union State Standards for "drinking water". In the case of biological analysis, we chose test organisms that were linked by the food chain: green protococcal algae, lower crustacea. In studying the action of the water samples on algae, the nature of the growth of the algae, intensity of their multiplication, and the value of the total production during the time of the experiment were determined. In experiments with lower crustacea, parameters were employed such as the survival of adult individuals and young ones, fertility of females, intensity of reproduction, number of individuals and formation of latent and abortive eggs in the female. In studying the influence of samples of the water to be tested on the fishes, we observed the changes in their erythropoiesis in a long experiment by use of the method of "acid erythrograms". As a result of the biological experiment, we found that the samples of investigated water varied in their effects on hydrobionts. Thus, for example, in studying the effects on these animals produced by water regenerated from human urine by the catalytic method, we found more pronounced changes in the erythropoiesis of fishes in comparison with the controls. However, 40 days after the start of the experiment, a gradual normalization of /220
the erythropoiesis level was observed, indicating the possibility of adaptation of the fish to the water under study.

In studying water samples obtained by the method of catalytic decomposition of hydrogen peroxide and water regenerated from moisture given off by fuel cells, different effects on hydrobionts were found, regardless of similar physical-chemical parameters. Thus, water obtained from hydrogen peroxide had an acute lethal effect on adult individual lower crustacea and their offspring. Water regenerated from moisture given off by fuel cells turned out to have a chronic lethal action on lower crustacea. The animals showed a decrease in the intensity of multiplication and molting, the females developed abortive eggs and offspring and there was a predominance of males among the offspring.

All of this indicates an unfavorable influence of the water under test on lower crustacea. In investigating the influence of water obtained from peroxide on unicellular protococcal algae, a change in the shape of the growth curve of the algae was observed which indicated a significantly reduced total biomass of the algae in comparison with the controls. This is indicative of the fact that the water under test was an unfavorable medium for normal growth and development of the algae. Similar results were obtained in experiments with higher water plants. In an experiment with fish living for 30 days in the water under test, a more significant influence on the erythropoiesis of the animals was found to be caused by the water obtained by the method of catalytic decomposition of hydrogen peroxide. Thus, the statistical index of the degree of influence of the water obtained from hydrogen peroxide was 52%, while the strength index of the influence of tap water was 20%.

Hence, biological experiments demonstrated the different effects of samples of investigated water on hydrobionts, although all of the sanitary and hygienic parameters of the water corresponded to the All-Union State Standard. This indicates the need for additional physical and chemical analysis as a check on the quality of water by biological analysis.

Method of Lyophilization

In order to determine the suitability of water for drinking when the water is regenerated from urine by the lyophilization method, toxicological investigation was carried out in addition to chemical analysis.

The study of the influence of regenerated water on the organism in an acute experiment showed that in the case of Daphnia rubra, lifetime and ability to reproduce in the lyophilic water was practically the same as for the controls:

| Water | Lifetime, Days | Multiplication |
|---|---|---|
| Reservoir | 6 | + |
| Tap | 6 | + |
| Distilled | 4 | - |
| Lyophilic without purification | 6 | + |

The results obtained are confirmed by tests involving isolated frog hearts: /221

| | Duration of Contraction of Heart, minutes |
|---|---|
| Control (physiological solution) | 65 ± 3 |
| Lyophilic water without purification | 47 ± 4 |
| Lyophilic water with purification using KU-2 resin | 55 ± 4 |

TABLE 50.* COMPARATIVE SANITARY-HYGIENIC EVALUATION OF WATER OBTAINED FROM URINE USING METHODS OF VACUUM DISTILLATION, CATALYTIC OXIDATION AND LYOPHILIZATION

| Parameters | Catalytic oxidation | | | Lyophilization | | | Vacuum distillation | | | Control (tap water) |
|---|---|---|---|---|---|---|---|---|---|---|
| | Prior to enrichment | | After enrichment | Prior to enrichment | | After enrichment | Prior to enrichment | | After enrichment | |
| | $M \pm m$ | P, % | | $M \pm m$ | P, % | | $M \pm m$ | P, % | | |
| Odor, points | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Taste, points | 0 | 0 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0—1 |
| Chromaticity, degrees | 5 | 0 | 5 | 5 | 0 | 5 | 10 | 0 | 10 | 10 |
| Transparency, cm | 30 | 0 | 30 | 30 | 0 | 30 | 30 | 0 | 30 | 30 |
| pH | 6,0±0,1 | 1,7 | 7,0—8,0 | 6,0±0 | 0 | 7,0—8,0 | 5,5±0,4 | 7,3 | 7,0—8,0 | 7,0—8,0 |
| Total hardness, mg·eq/l | 0,83±0,08 | 9,6 | 3,6 | 0 | 0 | 3,7 | 0— traces | 0 | 5,48 | 3,0 |
| Calcium, mg/l | | | | | | | | | | |
| Magnesium, mg/l | 0 | 0 | 64,5 | 0 | 0 | 65,2 | 0— traces | 0 | 92,1 | 39,6—44,0 |
| Chlorides, mg/l | 0 | 0 | 4,8 | 0 | 0 | 7,1 | 0 | 0 | 10,7 | 8,51 |
| Sulfates, mg/l | 14,04±0,04 | 0,28 | 160,0 | 31,4±1,3 | 4,1 | 145,2 | 6,5±0,53 | 8,3 | 159,7 | 9,9 |
| Total alkalinity, ml | 0,16±0,015 | 9,4 | 23,5 | 9,9±0,35 | 3,5 | 23,2 | 24±0,2 | 8,3 | 22,09 | 25,45 |
| Potassium, mg/l | 0,1 | 0 | 2,1 | 0,2 | | 2,2 | 0,1 | 0 | 2,1 | 2,3 |
| Sodium, mg/l | 4 | 0 | 20,1 | 4 | 0 | 20,2 | 4 | 0 | 20,3 | 4,0 |
| Fluorine, mg/l | 4 | 0 | 145 | 4 | 0 | 147 | 4 | 0 | 150 | 4,0 |
| Iodine, micrograms/l | 0,1 | 0 | 1,2 | 0 | 0 | 1,1 | 0,1 | 0 | 1,2 | 0,1 |
| Permanganate oxidizability, mg $O_2$/l | 0 | 0 | 10 | 0 | 0 | 9 | 0 | 0 | 10 | 5 |
| | 1,54±0,09 | 5,8 | 1,6 | 3,2±0,3 | 9,4 | 3,25 | 2,7±0,3 | 9,9 | 2,7 | 3,56 |
| Ammonical Nitrogen, mg/l | 0,11±0,003 | 2,7 | 0,12 | 2,3±0,13 | 5,7 | 2,4 | 0,1 | 1,7 | 0,12 | 0,2 |
| Nitrites, mg/l | 0,0021±0,0002 | 9,5 | 0,0025 | 0,013±0,0008 | 6,6 | 0,015 | 0,027±0,02 | 7,4 | 0,03 | 0,03 |
| Nitrates, mg/l | 0,1±0,04 | 4,0 | 0,12 | 0,14±0,01 | 7,1 | 0,15 | 0,17±0,016 | 9,4 | 0,18 | 0,3 |
| Phosphates, mg/l | 0,03±0,003 | 3,7 | 0,009 | 0,012±0,0007 | 3,9 | 0,0015 | 0,029±0,0028 | 9,6 | 0,03 | 0 |
| Uric acid, mg/l | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Creatinine, mg/l | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Urea, mg/l | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Microbial count, microbes/ml | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

*Note: Commas indicate decimal points.

As we can see from these data, the contraction time of the frog heart in regenerated water without preliminary purification decreased slightly in comparison with the controls. However, following purification of the water using sorbents, the values in the lyophilic water approached the control figures.

The absence of toxic action on the organism caused by regenerated water was also evident in an acute experiment on dogs involving intravenous injection of a physiological solution prepared using lyophilic water.

As we can see from the data presented below, the physiological parameters for the dogs were unchanged after the test:

| | Before Experiment | After Experiment |
|---|---|---|
| Body temperature, °C | 39 | 39 |
| Pulse, beats/minute | 60 | 60 |
| Respiration, breaths/minute | 21 | 30 |
| Hb, % | 12 | 12 |
| Leucocytes | 9,100 | 9,300 |

In addition to these studies, the gonadotropic activity of regenerated water was studied by injecting it into white mice. The experiments were performed on immature females using the method of Ascheim-Zondek in the modification of M. M. Zavadskiy. The reaction was read after 76 hours. It was found that in both the experimental and control animals the reaction was negative. Hence, the autopsy of the mice revealed no changes in the uterus, vagina or ovaries. This indicates that lyophilic water has no gonadotropic activity.

In a subacute experiment, we studied local and general effects of water regenerated by the lyophilic method on the mucous membranes of the eye and the tissue of the rabbit for a month. As a result of these studies it was confirmed that the effect of regenerated water was the same as in the controls.

The studies of the influence of water on the organism of white rats in a chronic experiment (90 days) showed that the animals willingly drank water regenerated by the lyophilic method, developed properly and gained weight. No changes in the dynamics of any physiological parameters were observed in the experimental animals with respect to the controls (Table 51).

A study of blood sugar in the rats after giving them a galactose load also failed to reveal any differences between the experimental and control groups. The slight deviations that were observed (in mg %) did not go beyond /222 the limits of the corresponding physiological norm.

| | Background | 3 months |
|---|---|---|
| Control | 159 ± 13.8 | 153 ± 13 |
| Experimental | 172 ± 10 | 180 ± 20 |

TABLE 51.* PHYSIOLOGICAL PARAMETERS IN EXPERIMENTAL ANIMALS USING WATER REGENERATED BY THE LYOPHILIZATION METHOD

| Water | Hb, % | | Leucocytes, thousands | | Body weight, grams | | Respiration rate, breaths/minute | |
|---|---|---|---|---|---|---|---|---|
| | Background | 3 months | Background | 3 months | Background | 3 months | фон | 3 месяца |
| Lyophilic | 13,3±1,0 | 13,6±0,9 | 13,2±0,9 | 10,8±1,3 | 100±10 | 245±10 | 91±5 | 80±6 |
| Control | | | | | | | | |
| Tap | 13,1±1,1 | 13,4±1,3 | 11,8±0,8 | 11,3±1,1 | 110±15 | 250±5 | 92±3 | 92±4 |
| Distilled | 12,8±1,2 | 13,0±1,1 | 11,2±0,9 | 11,4±1,0 | 105±12 | 242±9 | 96±3 | 95±5 |

*Note: Commas indicate decimal points.

We know that one of the sensitive parameters that respond to the toxic action on the organism is a change in the function of the adrenals which takes the form of a drop in their ascorbic acid content (Lubern, 1958). The functional state of the adrenals in experimental animals was studied by means of the Torn test. As we can see from the data presented below, the ascorbic acid content (in mg %) in the adrenals of experimental and control rats did not differ significantly:

| Water | Before administration of ACTH | After administration of ACTH |
|---|---|---|
| Tap | 430 ± 160 | 515 ± 120 |
| Distilled | 435 ± 152 | 400 ± 132 |
| Lyophilic | 356 ± 120 | 506 ± 122 |

Determination of the swimming time of animals with a load and survival time in a closed space was carried out by the method generally employed. The data in Table 52 indicates a lack of difference between these parameters in the experimental and control groups.

The absence of a toxic effect of regenerated water on the organism was confirmed by a subsequent pathomorphological study of organs and tissues of rats that use regenerated water for a long period of time. /223

Hence, an analysis of these experimental data on the toxicological evaluation of water regenerated by the lyophilic method indicates that both single and repeated use of such water had no unfavorable effects on animal organisms. In this connection, the method of regeneration of water by using lyophilization of wastes may be recommended for the development of reliable water regeneration systems to obtain water from products of human vital activity with a high degree of contamination.

TABLE 52. SWIMMING TIME OF ANIMALS WITH A LOAD AND SURVIVAL TIME IN A CLOSED SPACE

| Water | Swimming time, minutes | Survival time, minutes | Analysis of gaseous medium at the time of death, mg/liter | |
|---|---|---|---|---|
| | | | $O_2$ | $CO_2$ |
| Control | | | | |
| Tap | 8 ± 0.8 | 55 ± 4 | 8 | 12.5 |
| Distilled | 10 ± 1.0 | 48 ± 5 | 9 | 11.5 |
| Lyophilic | 8 ± 0.4 | 45 ± 3 | 8 | 12.5 |

Pathomorphological studies of the organs and tissues of animals that had drunk water regenerated from urine by the method of lyophilization were performed. 45 animals were used for these pathomorphological studies. They were divided up as follows into experimental groups:

| Time of Experiment | Lyophilic | Tap | Distilled |
|---|---|---|---|
| 1 month | 10 | 5 | 5 |
| 2 months | 5 | - | - |
| 3 months | 5 | 5 | 5 |
| Total | 20 | 10 | 10 |

The large number of animals used for the pathomorphological tests was necessary in order to obtain a statistically reliable group of results when studying adrenal glands, primarily the thyroid gland.

All of the animals, after being killed by ether, were autopsied and their internal organs subjected to microscopic examination. During the autopsy, the relative weight of the thyroid gland and adrenals were determined. The thyroid gland, adrenals and thymus were microscopically examined in all animals. Other internal organs such as the brain, heart, lungs, liver, spleen, kidneys, stomach, intestine, pancreas, and testicles were studied in six animals in a /224
"lyophilic group", and the pituitary was studied in three. In other groups, the internal organs were studied selectively, so that in the "distilled water" group emphasis was placed on the structure of the stomach and intestine. The organs were fixed in 10% neutral formalin, with sections being prepared in paraffin. The organ sections were stained with hematoxylin-eosin, while the thyroid was also studied according to Selye to determine the fuchsinophilic substances; the brain was studied according to Nissl. The sections of the adrenals and liver, obtained with a freezing microtome, were stained with scarlet red.

In the microscopic study, no changes were found in the structure of the internal organs of either the experimental or control animals. Calculation of the mean arithmetic values of the relative weight of the thyroid gland by

groups of animals showed insignificant differences which were attributed to the original condition of the animals. Thus, following a three-month experiment, in the lyophilic water group the mean arithmetic value of the relative weight of the thyroid gland in percent was 0.010% (with variations of 0.014-0.008), while for the tap water group it was 0.013% (0.012-0.007) and for distilled water it was 0.010% (0.011-0.09).

Microscopic Study of Endocrine Glands

The study of the structure of the thyroid gland in experimental animals showed that the follicles in the peripheral portions were of large size while the epithelium investing them was flat. The colloid in these follicles was stained intensively by eosin, while treatment by the Selye method resulted in a fuchsinophilic red color for the mass that could be seen against the green background of the remaining colloid. Follicles in the central parts of the gland were smaller in size and their epithelium was mainly cuboidal. The lumina of the follicles contained colloid that was only lightly stained by eosin. Between the peripheral and central parts there was a small zone with an intermediate type of follicle. The stroma of the thyroid gland was usually filled with blood and the capillaries between the follicles were over-filled with blood. Some animals showed small accumulations of lymphoidal cells. A more homogeneous structure of the follicles of the thyroid gland could be seen in the pedigreed rats. In these animals the colloid was stained more uniformly, and the epithelium of the follicles had almost the same depth everywhere. The same structure of the thyroid gland could be seen in the animals in the tap water group. In those animals which drank distilled water for three months, against a generally similar picture of the structure of the thyroid gland the follicles frequently showed a flattening of the epithelial cells. To check this observation, an ocular and objective micrometer was used to measure the height of the cells of the follicular epithelium of the thyroid gland in all the animals in the three-month experiment. In each group, the /225
height of 60 epithelial cells in the follicles located in the central part of the thyroid gland was measured.

The statistical evaluation of these results showed insufficient differences between the values obtained. Consequently, the impression of a thickening of the epithelial cells of the follicles in the animals of the distilled water group cannot be considered a reliable factor.

The structure of the adrenals of those animals which drank lyophilic water failed to show any changes with respect to the normal picture. The layers of the adrenals could be differentiated clearly and the cortical substance showed the venous sinuses to be filled with blood. Staining with scarlet red revealed moderate to significant changes in the lipide content. Weighing the adrenals also failed to reveal any differences between the animals in the lyophilic water and the control groups. The thymus and testicles also showed ordinary structures. The isles of Langerhans in the pancreas were clearly evident and consisted of groups of bright cells whose protoplasm was not stained by either eosin or hemotoxylin. When the pituitary of the experimental animals was studied, the same ratios of eosinophilic, basophilic and chromophobic cells were found as in the adenohypophysis of the animals in the tap

water group. The structure of parts of the hypophysis -- the intermediate lobe and the neurohypophysis -- were the same in the experimental animals as in the controls.

Microscopic Structure of Other Internal Organs of the Experimental Animals

The brain showed a moderate plethora of blood and perivascular edemas, individual cells with hyperchromic protoplasm, and nucleii whose boundaries were uneven. In the heart, small areas of muscle fibers were more strongly stained by eosin. The vessels of the myocardium were moderately plethoric and around the arteries one could see a slight stratification of the cell structure by edmatous fluid. The lungs of the experimental animals showed plethora of the venous vessels and occassionally the interalveolar capillaries as well. The lumina of the alveoli were dilated and airy. Around the bronchi and along some of the vessels, one could see accumulations of lymphocytes. The liver tissue was moderately plethoric; the intermediate capillaries located near capsules were somewhat more strongly dilated with blood. The protoplasm of the liver cells was pink; the nucleii were round and bright blue. When staining with scarlet red, groups of liver cells containing small and larger drops of fat could be seen around the central veins in some animals.

The follicles of the spleen in the experimental animals, mainly, contain /226
small amounts of lymphocytes, but some follicles retain a normal structure. The pulp of the spleen was frequently plethoric. In the kidneys, pronounced plethora was observed at the boundary between the cortical and medullary layers. The glomeruli had a normal structure. The protoplasm of the cells of the convoluted tubules had a fine granular structure and the nucleii were oval or circular in shape. The lumina of the straight canals were empty.

Microscopic investigation of the internal organs of the animals in the tap water group and the distilled water group showed the same pattern for the structure of the brain, heart, lungs, kidneys, liver and spleen as were observed in the animals fed lyophilic water for a long period of time.

The changes that occurred which could be detected by microscopic examination of the internal organs (perivascular edema in the brain and hyperchromatosis of individual gangliar cells, edema of the intermediate tissue of the myocardium around the heart, and eosinophilia of portions of the muscle fibers of the latter, differences in the plethora of individual organs of animals) showed an acute pattern and in all probability are a consequence of the fact that the animals were killed by ether. The changes mentioned earlier could not be linked to the harmful effect of lyophilic water.

The structure of the stomach and intestine in the animals of the lyophilic and distilled water groups showed no important changes of any kind with respect to the normal picture. The degree of desquamation of cells from the upper part of the mucous membranes in these animals was the same as the desquamation of cells in animals of the control groups.

Hence, the results of the pathomorphological studies indicate that experimental animals which had drunk lyophilic water showed no changes in either the

structure of the endocrine glands (thyroid gland, adrenals, thymus, isles of Langerhans, testes, pituitary) or other internal organs (brain, heart, lungs, liver, stomach, intestine, spleen, kidneys).

Vacuum Distillation

We know that some authors have pointed out the theoretical possibility of using vacuum distillation of urine to produce potable water (Nefedov, 1961; Konikoff, 1963).

Very detailed sanitary and hygienic studies were performed in 1961 by Nefedov, including a stage of evaluation of the regenerated water by human beings. However, the studies of the possibility of animals and human beings using water regenerated by this method were performed, as a rule, under strictly controlled experimental conditions and did not provide for complete enrichment of the water with mineral components. In this connection, in order to be able to recommend this method for planned spacecraft together with the development of optimum technological conditions for purification of this water, it was necessary to carry out comprehensive sanitary and toxicological testing. The data presented above indicate that it is possible to obtain potable water from urine by vacuum distillation and to ensure that this water has high hygienic parameters, only if it is subjected to additional purification with sorbents and enriched with mineral components (see Table 50). /227

However, the final conclusions regarding the degree of harmlessness of the water to the organism can be drawn only on the basis of an analysis of the data obtained in acute, subacute and chronic experiments on animals. For this purpose, we performed studies in an acute experiment on daphnia (Daphnia rubra) and isolated frog hearts using the generally accepted method (Drachev, 1956; Kravkov, 1911). The experiments were performed by us on 20 individuals of each species, using water from a reservoir or physiological solution as the control.

In the subacute experiment we studied local and general effects of regenerated water on the rabbit organism (six animals) in the course of a month, using a generally accepted method (Moiseyev, 1952).

In a chronic experiment we studied the prolonged influence of enriched regenerated water on the organism of white rats when given orally for six months. The experiments were performed on 60 animals with an initial weight of 140-170 grams, with 20 individuals in each of the experimental and control groups. The control animals obtained tap water or distilled water that was enriched. In addition to the regular observations of the external appearance and weight of the animals, the following physiological parameters were studied:

a) a general analysis of the blood, including the determination of the numbers of leucocytes, neutrophils with segmented nuclei, lymphocytes, monocytes, eosinophils and reticulocytes;
b) osmotic resistance of the erythrocytes;
c) phagocytic activity of the leucocytes;
d) activity of thymol (SH)-groups of blood serum;

e) antitoxic function of the liver (test with hexanal blue);
f) enzymatic activity of the alkaline phosphatase of potassium;
g) pathohistological examination.

All physiological parameters were studied using generally accepted methods described earlier. The analysis of the data obtained in the acute experiment indicated a practical absence of any kind of toxic effects on the organism. Thus, for example, the survival time of Daphnia rubra in the regenerated water was five days, while it was four days in tap water and six days in water from a reservoir. A slight decrease in the survival time in tap water possibly had something to do with its considerable chlorination during this season of the year. Likewise, no decrease in the survival time of the frog heart in the regenerated water was observed: (58 ± 3) minutes in comparison with the controls (66 ± 4) minutes. The lack of toxic effects of regenerated water prepared by the vacuum distillation method, due to its local or general effects on the organism, could be seen when it was studied in a subacute /228
experiment on rabbits. Thus, for example, during the entire experiment neither the experimental nor control group showed any change in the general appearance of the animals and no pathological reaction involving the mucous membranes of the eye, the skin and surrounding tissues was observed. The resorption time and value of the subcutaneous infiltrate in response to the administration of the experimental and control solutions was the same -- (2 ± 0.5) minutes and (3 × 4) cm.

Particular interest surrounded the study of the influence of regenerated water on the animal organism when used for a long time. The chronic observation of rats showed, for example, that under the influence of six months' absorption of enriched regenerated water no negative effects of any kind on the general condition were observed; the weight of the animals and the investigated physiological parameters remained the same.

At the same time, there was a slight change in the dynamics of some hematological parameters (segmented-nuclear leucocytes, lymphocytes, eosinophils, ORE) and the weight of the rats during the period of intensive growth in the experimental group of animals in comparison with the controls (Table 53). For example, when the white blood formula was studied, there was no significant difference in the total number of leucocytes during the entire experiment in either the control or experimental groups of animals. At the same time, however, slight changes in the percentile composition of individual components of the leucocytic formula were seen in the experimental animals in comparison with the controls. Thus, in the sixth month of the experiment, all control /229
animals showed a regular increase in the number of leucocytes with segmented nuclei in comparison with the background data. This was accompanied by a parallel decrease in the number of lymphocytes in the same group of rats. Similar changes in the leucogram are characteristic, as we know of seasonal variations in the blood picture. However, those animals that are given water to drink that has been regenerated by the method of vacuum distillation fail to show any significant variations in the numbers of the above mentioned elements of the blood. In addition, in contrast to the controls, where a regular increase in the percentage of monocytes was noted during the experiment, the experimental group of animals showed a decrease in their number at the beginning of the experiment in comparison with background values.

TABLE 53.* DYNAMICS OF CERTAIN PHYSIOLOGICAL PARAMETERS IN EXPERIMENTAL ANIMALS WHICH FOR SIX MONTHS WERE GIVEN WATER ENRICHED WITH SILVER (0.1 mg/liter) AND REGENERATED BY THE METHOD OF VACUUM DISTILLATION

| Parameters | Regenerated, enriched water | | | Tap water | | | Distilled wat | |
|---|---|---|---|---|---|---|---|---|
| | Background | 4 months | 6 months | Background | 4 months | 6 months | Background | 4 month. |
| Leucocytes, thousands | 13,5±0,7 | 12,8±1,1 | 10,1±1,2 | 15,7±1,5 | 14,9±1,0 | 14,5±1,4 | 12,6±0,4 | 14,6±1,2 |
| Leucocytes with segmented nuclei, % | 18,2±1,4 | 16,3±0,9 | 16,8±0,3 | 20,9±1,8 | 21,5±2,2 | 23,2±0,6 | 19,3±1,1 | 18,0±1,5 |
| Lymphocytes, % | 75,7±1,7 | 76,5±1,8 | 72,7±2,0 | 71,5±1,2 | 71,3±2,3 | 66,3±2,7 | 75,7±0,9 | 74,7±1,8 |
| Eosinophils, % | 1,7±0,3 | 4,5±0,6 | 3,2±0,2 | 3,8±0,8 | 3,5±0,9 | 3,5±0,2 | 4,0±1,0 | 2,2±0,7 |
| Reticulocytes, individuals | 24,4±3,8 | 22,5±1,8 | 32,6±8,1 | 20,3±2,0 | 18,2±2,4 | 38,0±4,9 | 15,3±1,5 | 21,7±3,4 |
| Weight, grams | 201±4,7 | 286±8,3 | 468±13 | 217±6,4 | 295±9,2 | 456±15 | 215±6,0 | 297±4,9 |
| Phogocytic activity of leucocytes, % | 5,4±0,45 | 6,3±0,6 | 6,3±0,8 | 5,0±0,9 | 7,2±1,0 | 5,3±0,7 | 6,1±0,8 | 5,0±0,8 |
| Phagocytic number, indiciduals | 0,08±0,02 | 0,11±0,019 | 0,125±0,005 | 0,1±0,02 | 0,12±0,01 | 0,16±0,11 | 0,08±0,01 | 0,12±0,0 |
| SH-groups of blood plasma, mM SH/ml | 59±5,6 | 60±2 | 65±3 | 50±3,9 | 51±1 | 54±2 | 54±2,2 | 55±2 |
| Hexanal anesthesia, minutes | 38±3 | 37±1 | 38±1 | 36±1 | 36±3 | 36±2 | 38±2 | 37±1 |

*Note: Commas indicate decimal points.

However, these changes were not permanent; by the second month of drinking the regenerated water there was a return to normal of the monocytes in these animals. In estimating the eosinophils, in contrast to the control animals, the "Rodnik" group showed a pronounced tendency toward an increase in their numbers with time. Such eosinophilia indicated that there was a slight allergization of the animals that were fed the regenerated water. Similar changes in the experimental animals in comparison with the controls were noted in respect to the red blood, for example, the osmotic resistance of the erythrocytes (ORE). While during the first few months there was a decrease in ORE in both the experimental and control groups of rats and seasonal variations could be detected, this correlation broke down later. Thus, for example, normalization of ORE in animals that had received tap water occurred by the fourth month of drinking, while in the group of animals that received /230
the regenerated water it was still somewhat less than background values by the end of the sixth month of the experiment.

In summarizing all this we must conclude that some of the changes in the dynamics of the individual hematological parameters observed in the experimental animals in comparison with the controls were not reliable and did not as a rule go beyond the limits of the corresponding physiological standards. They can be explained by adaptation of the organism to a new environmental factor, in this case the regenerated water; this is supported by similar examples under natural conditions (Barbashova, 1963). Thus, an analysis of the hematological parameters of the animals in the chronic experiment indicated a practical absence of any toxic effects on the organism caused by the prolonged usage of the regenerated water. Similar conclusions can be drawn from a study of other physiological parameters in the animals. Thus, for example, a determination of the phagocytic activity of leucocytes in rats did not show any marked differences between the experimental and control groups during the experimental period (see Table 53).

The tendency toward an increase in the number of microbes in animals in the experimental group was insignificant and fell within normal limits (Volkova, 1965). This indicated that the immunobiological reactivity of the organism of the experimental animals did not change under the influence of prolonged utilization of water regenerated from urine. The lack of a general toxic effect of water was supported also by the study of the decontaminating function of the liver by means of the hexanal test and the activity of sulfhydryl groups in the blood plasma. As we can see from the data in Table 53, the duration of hexanal anesthesia in experimental animals was practically the same as in the controls. The activity of the sulfhydryl groups in the blood plasma also did not change during drinking of regenerated water by the animals and corresponded to the physiological norm for that species of animal. In studying the activity of alkaline potassium phosphatase, no differences in the fermentative activity of the intestine were found between the experimental and control groups of rats, indicating a lack of a pathological influence of water regenerated with this device on the gastrointestinal tract in the course of prolonged usage. One is struck by a marked drop in alkaline phosphatase activity in all animals in the course of time. Thus for example, while the parameters on the basis of background data were 13 and 15,000 units in the control and experimental rat groups, by the end of the sixth month they had

dropped to 2 to 3,000 units. Such facts are in agreement with the data obtained by our laboratory in other experiments and can evidently be explained by changes due to age. Lack of a general toxic effect of water on the animals is also supported by subsequent pathomorphological studies of the organs and tissues at the end of 2, 4 and 6 months of experimentation. As we can see /231
from the data of the pathohistological examination, there were no changes in the experimental group of animals involving internal organs that indicated specific effects on the organism by the regenerated water. However, in examining the material, individual changes were found in the stomach, large and small intestine in the form of edema of the mucous membranes and extensive epithelial desquamation. In addition, there was strictly localized accumulation of pseudoeosinophilic leucocytes in the stroma of the mucous membranes of the stomach (at the point where the mucous membrane of the stomach of the rat merges with the pancreas). These changes were found in the experimental and control animals and were obviously linked to the digestive infiltration.

The mitotic activity of the epithelium in the gastrointestinal tract that was found in microscopic examinations and accompanied an increase in the number of scyphiform cells varied in different animals and was evidently a function of individual characteristics of the rats. Vascular problems in the tissues of the liver and spleen were found in almost all experimental and control animals and evidently caused their death. Hence, some pathological changes in organs and tissues were observed in all the animals, including the controls, and had nothing to do with the experiment.

The data which we obtained on the basis of a complex sanitary and hygienic evaluation of water regenerated from urine by the method of vacuum distillation, including toxicological studies on animals, therefore indicated a lack of negative influence of this water on the organism and demonstrated the feasibility of introducing this method in water-supply systems designed for long space flights.

This section contains data on a pathohistological investigation of animals that were given enriched water to drink which had been regenerated from urine by the methods of vacuum distillation and sorption from a condensate of atmospheric moisture. As controls, we used animals that were given tap water or distilled enriched water. Examination of the internal organs of rats during an autopsy failed to show any differences between the experimental animals of the various groups and in experiments of varying duration. By the fourth and sixth month of the test the rats were large and showed signs of aging. In order to shorten the presentation, we are providing data on the histological examination of the animals following the sixth month of the experiment.

Histological Examination of the Control Group of Animals[3]

Stomach. The stomach of the rat is divided into two parts: the rumen, which is lined with several layers of flat keratotic epithelium, and the stomach, which is lined with glandular epithelium. None of the control animals showed any changes in the structure of the stomach. The mucous membranes of the rumen were pleated. The epithelium was arranged in 5-6 rows, and the /232
layers could be distinguished clearly: basal, glyciform, granular and keratic.

[3]Translator's Note: autopsy notes listing observations as made. /

The keratic layer was thick, laminar and desquamated into the lumen. The basal layer was located on the basal membrane. In the submucous layer, there was slight accumulations of pseudoeosinophilic leucocytes, with slightly more at the juncture with the glandular epithelium.

At the point where the multilayered flat keratosic epithelium blends into the vascular, the vascular tubules are lined with large bright cells with a foamy protoplasm, reminiscent of the cells in the cervical portion of the gland. One can distinguish the cell forms that form the mucous membrane of the gland (cylindrical, main, supplementary, cervical and coating cells). The coating cells cannot always be seen clearly, since they are rapidly subjected to autodigestion. In the stroma of the mucous membrane of the stomach, groups of pseudoeosinophilic leucocytes and lymphocytes can be found. Mitoses are quite often found in the cervical region of the stomach. Their numbers differ in various animals. The muscle layers of the gastric wall have no particular features. There is moderate plethora of all layers of the gastric wall.

Small intestine. The mucous membrane of the small intestine retains its structure. The fringed epithelium, invested with villi, is highly desquamate, so that the villi are not covered with epithelium for the entire length. The epithelial crypt is retained. The villi are shortened and thickened toward the distal part of the gastrointestinal tract. The number of scyphiform cells in the epithelium lining the small intestine is also increased in this direction. The number of scyphiform cells differs in individual animals. The fringed epithelium of the mucous membrane contains a great many mitoses. The mitotic activity of the epithelium of the small intestine shows an individual nature. In the stroma of the villi there are quite a few pseudoeosinophilic leucocytes and mononuclears, but their numbers differ in different animals. In the stroma of the mucous membrane, lymphoid follicles have been found, and sometimes there are very large accumulations of them (nuclear plates). The submucous and muscular layers have no particular features; the entire wall of the small intestine is moderately plethoric.

Large intestine. The mucous membrane of the large intestine is folded. The epithelium of the large intestine is always well preserved. Many scyphiform cells. Their numbers increase in the caudal portion of the intestine. The epithelial cells frequently show figures of mitosis. Not all individuals have the same number of mitoses. Pseudoeosinophilic leucocytes are found in the stroma of the mucous membrane. Moderate plethora of all layers of the intestinal wall. Submucous and muscle layers show no particular features.

Pancreas. All cell structures of the pancreas are clearly visible. The acinuses are filled with zymogen. The lumina of the passageways in the gland are patent. The cells of the incretory apparatus show no particular features.

Liver. Pronounced plethora of liver tissue, with scattered hemorrhages. /233
Central veins distended and plethoric. Protoplasm of liver cells granular. The nuclei of some cells are large and bright (stimulating cells). Mononuclear infiltration around the triads. Epithelium of bile ducts proliferated and constricted. Some animals show focal death of cells and an increase in the amount of connective tissue. Intensity of irritation of liver tissue differs.

Spleen. Plethora of red pulp. Follicles small, centers of reproduction small. Layer of bright cells clearly visible along the periphery of the follicles. Some animals show an increase in macrophages in the sinuses of the spleen and a breakdown of cellular elements. Megokaryocytes frequently found.

Histological Examination of the Experimental Group of Animals

Due to the fact that the various samples of experimental water did not affect the morphological structure of the gastrointestinal tract, pancreas, liver and spleen, we shall give a general description of the data obtained which characterize all experimental groups.

The histological picture of the mucous membrane of the pancreas and stomach of the rat were the same as described for the control group, and was the same for all groups of animals. The structure of the stomach wall was retained. The multilayered flat keratosic epithelium of the pancreas and the glandular epithelium of the stomach were clearly evident. There was a slight plethora of the stroma of the mucous membrane, containing groups of pseudo-eosinophilic leucocytes and lymphocytes. In the submucous layer the pseudo-eosinophilic leucocytes formed accumulations at the point where the pancreatic epithelium merges with the glandular epithelium. Mitoses were rarely found. The muscle layers showed no particular characteristics. In two instances there was significant desquamation of superficial epithelium and edema of the mucous membrane. One animal showed superficial ulceration of the mucous membrane at the transition between the pancreas and the stomach. In a small portion of the mucous membrane one could see one layer of cuboidal cells with succulent nuclei.

Small intestine. Histological examination of the small intestine failed to reveal any changes in comparison with the control group. The villi and crypts of the mucous membrane of the small intestine were clearly visible. In the stroma of the villi, the dilated vessels and a small amount of pseudo-oesinophilic leucocytes and mononuclears could be seen. There were frequent instances of mitosis in the fringed epithelium of the villi and crypts. The stroma of the mucous membrane showed groups of large lymphoid follicles. Not all the follicles showed centers of multiplication. The latter showed mitoses and breakdown of cells. Moderate plethora of all layers of the intestinal wall.

Large intestine. No unusual characteristics were seen in the structure of the large intestine in comparison with the control group. The mucous membrane had an ordinary structure. The epithelium showed frequent instances of mitosis. The stroma had friable connective tissue. The submucous and mucous layers showed no particular characteristics. /234

Pancreas. The tissue of the pancreas was plethoric and lymphostasis was evident. The cells of the acinuses were clearly evident. Central parts of the acinuses filled with zymogen. Secretory cells of the isles of Langerhans showed no particular characteristics.

Liver. Markedly plethoric, with hemorrhages into the hepatic blood. Dystrophic changes in liver cells. Cells found with friable large nuclei. Epithelium of bioducts proliferative, desquamating into the lumen of the ducts, forming plugs. Tissue infiltrated with mononuclears around the triad.

Spleen. Follicles of the spleen small, centers of multiplication in them small. Mitoses found rarely in the centers of multiplication. Around the follicles -- a layer of bright cells, around which many macrophages occur. Sinuses of red pulp dilated. Megokaryocytes found.

## Sanitary and Toxicological Evaluation of Water Regenerated From Urine By The Oxidation-Catalytic Method

In the course of developing a technique of regenerating water from urine by the oxidation-catalytic method, we performed a sanitary and toxicological evaluation of samples of such water obtained by various purification methods. We used water regenerated by the catalytic method without additional purification, as well as water that had been subjected to subsequent purification using sorbents. The survival time and the ability to multiply in water regenerated by the oxidation-catalytic method were investigated using Daphnia rubra:

| Conditions of Regeneration of Water | Survival Time | Multiplication |
|---|---|---|
| Furnace temperature 400°, without purification | 30 minutes | - |
| Furnace temperature 150°, without purification | 4 days | + |
| Furnace temperature 400°, with purification (KU-2 + $CaCO_3$) | 5 days | + |
| Control (tap water) | 6 days | + |

The study of the influence of regenerated water on the organism in an acute experiment showed that survival time and ability to multiply did not differ markedly from the controls in the case of Daphnia rubra in water that was obtained at a temperature of 150°, while there was a sharp decrease in the survival time of these crustacea in catalytic water obtained at a temperature of 400° without purification. Additional purification of the water by sorbents led to an increase in the survival time of the crustacea up to control values.

The results which we obtained in examining water by using Daphnia were also confirmed by a test with the isolated frog heart: /235

| Water | Duration of contraction of the heart, minutes, M ± m |
|---|---|
| Control (physiological solution) | 65 ± 3 |
| Catalytic, $t_{furnace}$ 400° | 29 ± 3 |
| Catalytic, $t_{furnace}$ 150° | 32 ± 3 |
| Catalytic, $t_{furnace}$ 150° with additional purification using KU-2 + $CaCO_3$ | 55 ± 4 |

As we can see, the shortest time of contraction of the frog heart occurred in catalytic water regenerated with a furnace temperature of 400°. In water regenerated with $t_{furnace}$ = 150° with subsequent purification on sorbents, the contraction time of the heart was increased, approaching control values.

The data which we obtained in the toxicological experiment were conformed by the results of a sanitary and chemical evaluation of samples of catalytic water from different purification systems. On the basis of an analysis of these data we can conclude that the optimum hygienic properties are exhibited by water regenerated from water with $t_{furnace}$ = 150° with purification on sorbents. In this connection, this technology for water purification was used as the basis for building a similar regeneration system in metal. Water obtained from this device was subjected to prolonged toxicological testing on animals with subsequent evaluation by human subjects in a one-year experiment.

Experiments on Animals

Toxicological evaluation of water regenerated by the catalytic method was performed on 50 large male rats for two months. Preliminary enrichment of the water with mineral components according to the method which we developed was carried out and the water was then decontaminated with a solution of silver ions at a concentration of 0.1 mg/liter. The 20 control animals received tap water or distilled enriched water.

To evaluate the influence of the water, we used the following tests:

- general clinical observation (external growth, development, weight);
- general toxic function of the liver (hexanal test);
- number of leucocytes in the peripheral blood;
- osmotic resistance of erythrocytes;
- number of free SH-groups in blood serum;
- phagocytic activity of leucocytes.

During the experiment the animals in the experimental group looked practi- /236
cally the same in external appearance, activity and weight increase as both of the control groups:

| Water | Background | After 1 month | Difference in weight | After 2 months | Difference in Weight |
|---|---|---|---|---|---|
| Control | 257.5 | 312.3 | +54.8 | 342.5 | +85.0 |
| Distilled + Ag | 252.0 | 330.7 | +78.7 | 367.1 | +115.1 |
| Catalytic | 272.4 | 331.1 | +58.7 | 366.9 | +94.5 |

To evaluate the antitoxic function of the liver, a test involving hexanal was used. The duration of hexanal anesthesia, in conjunction with the time required for breakdown of hexanal by the enzyme systems of the liver in animals which had received regenerated water, had increased by the first month

(24.2 ± 0.41 for the background of 39.5 ± 2.21) and remained at practically the same level until the end of the experiment (38.3 ± 2.67 by the end of the second month):

| Water | Background | After 1 month | After 2 months |
|---|---|---|---|
| Tap water | 24.2 ± 0.41 | 39.2 ± 4.84 | 42.0 ± 7.7 |
| Distilled water (enriched) | 24.2 ± 0.41 | 41.0 ± 4.79 | 31.5 ± 3.65 |
| Catalytic + Ag | 24.2 ± 0.41 | 39.5 ± 2.21 | 38.3 ± 2.67 |

However, the increase in the duration of hexanal anesthesia cannot be attributed to the influence of the experimental water on the animal's organism since an identical reaction to the hexanal test was observed in the control groups. The difference in the duration of hexanal anesthesia in the control groups in the second month of investigation was not statistically reliable.

The study of certain hematological parameters revealed that the number of leucocytes (in thousands per ml of blood) in the groups that received regenerated water containing silver ions frequently increased by the end of the first month of drinking, without going beyond the limits of the physiological norm, then dropped off toward the end of the experiment more significantly in the experimental group:

| Drinking time | Catalytic | Distilled (enriched) + Ag | Tap water |
|---|---|---|---|
| Background | 11.9 | 11.1 | 12.3 |
| 1 Month | 16.3 | 17.1 | 13.8 |
| 2 Months | 9.5 | 14.0 | 11.5 |

The number of leucocytes in the blood of animals that received tap water during the experiment varied insignificantly and remained practically constant. Hence, there were no differences in the dynamics of the hematological parameters in the experimental and control animals.

The study of the osmotic resistance of the erythrocytes revealed a slight /237
increase toward the end of the experiment in animals of all groups, with a slightly greater value for rats that received regenerated water. It is possible that this increase in the osmotic resistance of the erythrocytes has to do with aging characteristics of the animals.

The study of the content of sulfhydryl groups in blood serum of animals showed a slight increase in these values in rats that used regenerated and distilled enriched water in comparison with tap water. These changes were insignificant, however, and did not go beyond the limits of the corresponding physiological norm.

| Water | Background | In 1 month | In 2 months |
|---|---|---|---|
| Control | 55.8 ± 23 | 57.3 ± 1.98 | 56.0 ± 1.27 |
| Enriched distilled + Ag | 58.0 ± 2 | 57.3 ± 1.33 | 62.4 ± 2.02 |
| Catalytic | 57.27± 1.35 | 57.3 ± 1.33 | 62.0 ± 1.71 |

The study of the phagocytic activity of the blood leucocytes in the animals showed no significant differences between the experimental and control groups. The variations in the phagocytic activity during the experiment in all the groups were identical (Table 54).

TABLE 54.* PHAGOCYTIC ACTIVITY OF BLOOD LEUCOCYTES OF ANIMALS FOLLOWING DRINKING OF WATER REGENERATED BY THE CATALYTIC METHOD

| Water | Background | | | After 2 months | | |
|---|---|---|---|---|---|---|
| | Phagocytic activity M ± m | Phagocytic number | Phagocytic index | Phagocytic activity M ± m | Phagocytic number | Phagocytic index |
| Control | 3,41±0,5 | 0,08 | 0,33 | 5±1 | 0,11±0,023 | 0,36±0,245 |
| Distilled (enriched) + + AG | 3,41±0,6 | 0,08 | 0,33 | 4,2±0,65 | 0,07±0,014 | 0,33±0,12 |
| Catalytic | 3,21±0,7 | 0,08 | 0,33 | 4,66±1,58 | 0,1±0,033 | 0,66±0,77 |

*Note: Commas indicate decimal points.

Hence, on the basis of these data we can conclude that prolonged drinking of regenerated water from a catalytic device by experimental animals failed to produce any kind of changes in the organism that had to do with its toxic action.

The results we obtained in experiments on animals made it possible to move on to the next stage of the research, investigating the effects on man produced by water regenerated by the catalytic method.

Influence on the Human Organism of Water Regenerated by the Catalytic Method

In a long, one-year experiment, the subjects used water regenerated from /238
urine by the catalytic method for drinking and preparing food. This water was enriched by a specially developed method. An analysis of special questionnaires filled out by the subjects indicated a lack of significant complaints regarding the state of health on their part and nothing about the quality of the water that they used during this time. This was supported by data from systematically performed water analyses which indicated that the latter had high sanitary and hygienic qualities. From the data collected from a carefully performed check of the condition of the organism of each subject, it was also clear that the water that they used was completely satisfactory and failed

to produce any changes in the physiological functions of the organism. There were some changes, but they were not permanent and constituted reactions that were characteristic of a stay by human beings in a hermetically sealed chamber. All of this indicates that water regenerated from urine by the catalytic method and enriched with a broad spectrum of mineral components and trace elements according to a method which we devised has no negative effects on the human organism and promotes the normal conduct of vitally important functions of the organism in the course of its prolonged usage.

## CONCLUSION

The present work has dealt with only a few of the problems that arise in /239
the development of water supply systems. It was not possible to treat completely such problems as heat and mass exchange in regeneration systems, problems involving the design and reliability of water supply systems, etc. As regards the medical and biological aspects, we were able to deal only briefly with such important problems as the change in water-salt metabolism under the influence of spaceflight factors. These matters clearly must serve as subjects for special studies and publications.

In conclusion, it should be emphasized once again how complicated it is to develop systems for water supply that are based on regeneration processes. Thus, for example, despite the fact that 60 and 90-day tests of life-support systems have been carried out in the United States, American researchers working on the "Skylab" orbiting station have designed water supply systems based on water reserves with a total volume of 2.7 tons. Evidently the reliability problems are critical in this case.

This analysis of the data in the literature, as well as the discussion of a number of experimental studies, may be valuable in the design of water supply systems for spacecraft crews making journeys of varying duration which will involve their independent existence in flight.

## APPENDIX 1. DRINKING WATER STANDARDS

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| Parameters | USSR | USPHS | WHO | SSB |
|---|---|---|---|---|
| Physical | | | | |
| cloudiness | 2.0 | 5.0 | 5.0 | 10 |
| chromaticity, degrees | $\leq$ 20 | 15 | $\geq$ 50 | 15 |
| over, points | $\leq$ 2.0 | 3.0 | Not forbidden | Not forbidden |
| taste, points | $\leq$ 2.0 | -- | Not forbidden | Not forbidden |
| pH | 6.5-9.5 | -- | 6.5-9.2 | -- |
| Dry residue, mg/liter | | 500 | 500-1,500 | 1,000 |
| Inorganic Substances, mg/liter | | | | |
| $NH_3$ | -- | -- | 0.5 | -- |
| $NO_3^-$ | -- | 45 | 50 | 10 |
| $As^{3+}$ | 0.05 | 0.05 | 0.05 | 0.05 |
| $Ba^{2+}$ | -- | 1.0 | 1.0 | 2.0 |
| Cd | -- | 0.01 | 0.01 | 0.05 |
| Cl | -- | 250 | 350 | 450 |
| $Cr^{6+}$ | -- | 0.05 | 0.05 | 0.05 |
| Cu | 3.0 | 1.0 | 1.5 | 3.0 |
| F | 1.5 | 1.7 | 1.5 | 2.0 |
| Fe | 0.3 | 0.3 | 0.1 | Not forbidden |
| Pb | 0.1 | 0.05 | 0.05 | -- |
| Mg | -- | -- | 50-125 | 0.2 |
| Mn | -- | 0.05 | 0.1 | Not forbidden |
| Ag | -- | 0.05 | -- | 0.05 |
| $SO_4^{-2}$ | -- | 250 | 250 | 250 |
| Zn | 5.0 | 5.0 | 5.0 | -- |
| Total hardness, mg·eq/liter | 7.0 | -- | 2.0-10 | -- |
| Oxidizability, $O_2$ mg/liter | -- | -- | 10 | 100 |
| Total microbial count | $\leq$ 100 | -- | -- | 10 |
| Coli index | 2.0 | 2.2 | 1.0 | -- |

NOTE: USPH - United States Public Health Service. International Standards for Drinking Water. Geneva, 1964.
WHO - World Health Organization. International Standards for Drinking Water. Geneva, 1964.
SSB - Space Science Bureau (USA), "Aerospace Medicine", Vol. 38, p. 789, 1967.
USSR - All-Union State Standard 2874-54. Moscow, Standards Publishing House, 1969.

## APPENDIX 2. PHYSICAL AND CHEMICAL WATER CONSTANTS

/241

| | |
|---|---|
| Molecular weight | 18.016 |
| Temperature (at a pressure of 1 atm) | |
| Freezing | 0° |
| Boiling | 100° |
| Maximum density | 3.98° |
| Latent heat | |
| Melting (at 0°) | 79.7 calories/gram or 1.437 kcal/m |
| Vaporization at t = 0° | 597.3 calories/gram |
| t = 100° | 539 calories/gram |
| Thermal conductivity (in cal/cm·sec·degree) | |
| Liquid water at t = 0° | 0.00120 |
| Liquid water at t = 20° | 0.00143 |
| Liquid water at t = 75° | 0.00154 |
| Steam at t = 46° | 0.0000458 |
| Steam at t = 100° | 0.0000551 |
| Viscosity in centipoise at t = 20° | 1.002 |
| Cryoscopic constant | 1.85 |
| Ebullioscopic constant | 0.516 |
| Dielectric constant at t = 20° | 80.4 |
| Specific electrical conductivity at t = 25°, $ohms^{-1} \cdot cm^{-1}$ | $6.2 \cdot 10^{-8}$ |
| Ionic derivative of water at t = 20° | $0.86 \cdot 10^{-14}$ |
| Concentration of $H^+$ ions in pure water at t = 20°, g·ions/liter | $0.927 \cdot 10^{-7}$ |

## APPENDIX 3. METHOD OF DETERMINING OXIDIZABILITY OF WATER (Kul'skiy, 1963)

Permanganate Method

The permanganate method is one of the most popular and consists of the oxidation of substances by potassium permanganate during heating. Permanganate oxidizability is 40-50% of the true oxidizability of substances. Because it is a powerful oxidizer, $KMnO_4$ reacts with reducers contained in water. With a low chloride content oxidation occurs in an acid medium, while when the chloride content is high (100-1,000 mg/liter) it occurs in an alkaline medium.

In the acid medium, the reaction proceeds as follows:

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O.$$

In an alkaline medium, reduction proceeds only to $Mn^{4+}$.

Excess $KMnO_4$ reacts with oxalic acid introduced to the solution:

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ = 2Mn^{2+} + 10CO_2 + 8H_2O.$$

The oxalic acid, without entering into the reaction, is titrated with potassium permanganate.

Solutions used. 1. 0.01 n p-p oxalic acid.

2. 0.01 n p-p potassium permanganate. The solution must be stored in a dark container. Since 0.01 n solutions of potassium permanganate are unstable, their normality must be checked during each determination of the oxidizability. For this purpose, 100 ml of distilled water is heated to boiling, then acidified with sulfuric acid (10-15 ml, dilution 1:4), the flask is removed from the heater, precisely 10 ml of a 0.01 n solution of oxalic acid is added and titration is performed until a slightly pink color is developed in the potassium permanganate solution. The coefficient of normality of the solution of potassium permanganate is calculated by the formula /242

$$N_{KMnO_4} = \frac{10 \cdot 0.01}{W},$$

where W is the volume of the $KMnO_4$ solution which is consumed in titration.

3. Sulfuric acid solution (dilution 1:4). For oxidation of impurities, the $KMnO_4$ solution is added until a slightly pink color is obtained.

4. A concentrated caustic soda solution is prepared by dissolving 50 g of chemically pure NaOH, previously purified to get rid of the soda film by rinsing with distilled water. The caustic soda is originally dissolved in a

small amount of distilled water in a beaker, then transferred to a measuring flask (100 ml) and brought up to the mark. The cloudy solution is cleared by decanting or filtration.

Method of determination in an acid medium. 100 ml of the water to be tested is placed in a conical flask with a 250 ml capacity; 5 ml of a sulfuric acid solution in a 1:3 dilution is added after which exactly 10 ml of an approximately 0.01 n solution of potassium permanganate is added. After covering the flask with a watchglass or a funnel, the liquid is boiled for 10 min. Part of the permanganate added is consumed in oxidizing the organic impurities in the water. Then the flask is removed from the heater and exactly 10 ml of 0.01 n oxalic acid is added, after which it is shaken vigorously. The solution is decolored because the oxalic acid reduces the remaining potassium permanganate. The decolored hot solution is titrated with a 0.01 n solution of potassium permanganate until a slightly pink color is obtained.

The oxidability of the water (X -- in mg/liter $O_2$) is determined by the formula

$$X = \frac{[W_1 - (W_2 + W)]N \cdot E - 1{,}000}{W_3}$$

where $W_1$ is the total amount of 0.01 n solution of potassium permanganate added to the test tube for the determination (in ml);

$W_2$ is the amount of 0.01 n solution of potassium permanganate which is used in oxidizing the organic substances in the distilled water added to the test tube for diluting the water under test (in ml);

W is the amount of 0.01 n solution of potassium permanganate which is used to oxidize 10 ml of a 0.01 n solution of oxalic acid (in ml);

N is the coefficient of normality of the potassium permanganate solution;

E -- mg·eq $O_2$;

$W_3$ is the volume of water to be tested, collected for the determination (in ml).

Method of determination in an alkaline medium. 0.5 ml of a concentrated solution of NaOH is placed in a conical flask with a sample of water, using a pipette; it is then placed on a gauze square over a burner flame or on an electric hot plate. When boiling commences, exactly 10 ml $KMnO_4$ are added drop-by-drop to the test tube and boiled for 10 minutes, beginning with the appearance of the first bubbles. When this interval has elapsed the sample is removed from the heat, cooled to 60° and mixed with 6 ml of a $H_2SO_4$ solution (diluted 1:4); then a 0.01 n solution of oxalic acid is added from a burette until total decoloration is achieved. The sample is then titrated with $KMnO_4$ solution until a definite slightly pink color is obtained, in comparison with an equal volume of distilled water.

Bichromate Method

Determination of bichromate oxidability is based on the oxidation of organic substances contained in the dry residue of bichromic acid, with boiling in the presence of concentrated $H_2SO_4$. For improved oxidation of organic substances by the chromic method, it is carried out in the presence of a catalyst -- silver sulfate. The chromic acid, without entering into the reaction, is titrated with a solution of divalent iron salt: /243

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ = 2Cr^{3+} + 6Fe^{3+} + 7H_2O.$$

Solutions used. 1. 0.4 n solution of $K_2Cr_2O_7$ in sulfuric acid, prepared by dissolving 19.6 grams of chemically pure $K_2Cr_2O_7$ in 500 ml of distilled water, to which (after the $K_2Cr_2O_7$ is dissolved) 500 ml of chemically pure $H_2SO_4$ is gradually added (specific gravity -- 1.84). The $H_2SO_4$ is boiled beforehand to oxidize the organic substances contaminating it.

2. 0.2 n solution of mohr's salt $(NH_4)_2Fe(SO_4)_2$, prepared by dissolving 78.6 grams of the salt $(NH_4)_2Fe(SO_4)_2$ in distilled water, to which 20 ml of chemically pure $H_2SO_4$ (specific gravity -- 1.84) are then added and brought up to a volume of 1 liter.

3. A solution of diphenylamine is prepared by dissolving 0.5 grams of diphenylamine in 100 ml of chemically pure $H_2SO_4$ which is then poured into 20 ml of distilled water.

4. 0.1 n solution of $K_2Cr_2O_7$. Recrystallized $K_2Cr_2O_7$ is dried to a constant weight in a drying chamber at 180-200°. The resulting preparation is stored in a weighing bottle in a desiccator. Exactly 4.9020 grams of the preparation is weighed out and dissolved in distilled water in a measuring flask (1 liter).

5. Phosphoric acid is used (chemically pure, 80 or 60%).

6. $H_2SO_4$ solution (dilution 1:1).

7. Silver sulfate, $Ag_2SO_4$.

Method of determination. A specific volume of water is evaporated to dryness in a conical flask (100 ml). 10 ml of a 0.4 n solution of potassium dichromate in dilute 1:1 $H_2SO_4$ is added to the dry residue, after which 0.1 g of $Ag_2SO_4$ is added (the silver sulfate is added as a catalyst). The flask is closed with a stopper, heated and boiled for 5 minutes. After cooling, the

contents of the flask are washed out into a large conical flask (250 ml); this yields a fluid volume of 75 to 100 ml. 2.5 ml of phosphoric acid and 5 drops of diphenylamine solution are added to the resultant solution.

The chromic acid that remains after the organic substances in the water have been oxidized is titrated with a 0.1 n solution of mohr's salt until the dark blue color changes to green; this takes place very suddenly in the presence of phosphoric acid and is produced by one or two drops of a 0.1 n solution of mohr's salt.

The bichromate oxidability (X) is calculated by the formula:

$$X = \frac{(W_1 - W_2)N \cdot E \cdot 1{,}000}{W_3}$$

where $W_1$ is the volume of a potassium bichromate solution (in ml of solution of mohr's salt); $W_2$ is the volume of the solution of mohr's salt, used for titration (in ml); $W_3$ is the volume of water used for determination (ml); N -- normality of the mohr's salt solution; E -- mg·eq $O_2$.

Iodate Method

Potassium iodate in a sulfate solution of a specific concentration of sulfuric acid quantitatively oxidizes the organic substances. The carbon of the organic compounds is changed to carbon dioxide gas, the nitrogen to ammonium sulfate, the sulfur to sulfuric acid and the phosphorus to phosphoric acid.

Oxygen, which constitutes part of organic compounds, is consumed in the oxidation of these substances, but an insufficient amount of oxygen is split off from the potassium iodate. The reaction proceeds according to the equation

$$2IO_3^- + 2H^+ = I_2 + H_2O + 5O.$$

The amount of potassium iodate consumed in this oxidation shows the oxidability of the water which, as we already mentioned, reflects its content of organic and inorganic reducers.

Reagents /244

Potassium iodate, A. P.
Sulfuric acid, pl. 1.84
Crystalline potassium iodide.
Sodium thiosulfate, 0.01 n, 0.05 n or 0.1 n solution.

Method of determination. Using an analytical balance, the following amounts of potassium iodate are weighed out into a weighing bottle (with an accuracy of up to 0.1 mg): with oxidability from 5 to 20 mg/liter (on the basis of the oxygen), 12-15 mg; with oxidability from 20 to 150 mg/liter -- 50 to 100 mg; with oxidability above 150 mg/liter, 0.1-1 gram.

The contents of the weighing bottle are washed out into a round-bottom flask to determine the oxidability, carefully rinsing out the weighing bottle with distilled water. No more than 10 ml of water need be consumed in this fashion. Then 30 ml of sulfuric acid are added (pl. 1.84) and the contents are mixed well by carefully rocking the flask. Then 10 ml of the tap water to be analyzed is added to the flask by using a pipette and again carefully shaken. After the flask has been connected to a reflux cooler, it is gradually heated in a sand bath until it starts to give off violet iodine vapor, at approximately 170°. Heating is continued for another 0.5-1 hour (see supplementary note 1 below) until no more iodine vapor is given off and the contents of the flask become colorless and transparent. The flask is then disconnected from the cooler and 75 ml of distilled water is carefully poured into it down the walls. The solution may then be colored yellow by the dissolved iodine. In order to get rid of the iodine the solution is boiled without the cooler until the yellow color and the odor of iodine disappear. Then the flask is cooled, its contents transferred quantitatively into a measuring flask with 200-500 ml capacity, and an amount of distilled water is added to the solution up to the mark; the flask is then closed with a stopper and the contents thoroughly mixed.

One gram of crystalline potassium iodide is placed in a conical flask fitted with a ground glass stopper; 50 ml of distilled water is added after which an aliquot part of the solution to be analyzed is added from the measuring flask. After sealing the flask with a ground glass stopper, its contents are mixed and allowed to stand for 10 to 15 minutes in a dark place.

The separated iodine is titrated with a solution of sodium thiosulfate in the usual manner. If 12-15 mg of potassium iodate was added, a 0.01 n solution of thiosulfate is used for titration; if larger amounts of iodate were added, titration is performed with a 0.05 or 0.1 n thiosulfate solution. If the oxidability of the waste water is less than 70 mg/liter (calculated for oxygen), the entire contents of the round-bottom flask are used for titration without dilution in a measuring flask.

Then a "blank" test is run under exactly the same conditions, adding 10 ml of distilled water instead of the same amount of waste water.

Supplementary notes. 1. Addition of potassium iodate to the solution to be analyzed in the form of a precisely weighed out batch, without measuring the specific volume of the solution, is recommended here for the following reason. Since the sulfuric acid content in the solution must be at least 65%, when the oxidation process is carried out, more water cannot be added. Therefore, the potassium iodate concentration (if it is added in the form of a solution) must be at least 5%, which is 120 times greater than the concentration of the sodium thiosulfate solution used for titration (0.01 n). This

means that a deviation of 0.02 ml (a small drop) in measuring out the potassium iodate solution causes a corresponding change in the consumption of the thiosulfate solution in titration, amounting to 2.4 ml; in the determination of small quantities, this is unacceptable.

The weighed batch of dry potassium iodate may be replaced by a 5% or 10% solution of this substance only under the condition that the latter is added from a weighing burette, and weighed out with an accuracy of up to 1 mg.

2. The sulfuric acid content in the total mixture must be 65-80% by weight.

Calculation. Oxidability is expressed in mg of potassium iodate or oxygen required for total oxidation of all reducers in the water being analyzed and is calculated as follows:

$$X = \frac{(\frac{n \cdot m_1}{m_2} - a) \cdot K \cdot 0.3567 \cdot 1{,}000}{V}$$ /245

or

$$X_1 = \frac{(\frac{n \cdot m}{m_2} - a) \cdot K \cdot 0.06667 \cdot 1{,}000}{V},$$

where X is the oxidability (in mg of $KIO_4$/ml); $X_1$ is the oxidability (in mg $O_2$/liter of water); $m_1$ is the weight of potassium iodate which is added to the flask when analyzing the water (in mg); $m_2$ is the same for the "blind" test; a is the volume of sodium thiosulfate solution used for titration of the water sample being analyzed (in ml); n is the volume of the same solution consumed in titration in the "blind experiment"; K is the correction coefficient for adjusting the concentration of the thiosulfate solution to exactly 0.01 n (or 0.05 n, 0.1 n if solutions of these concentrations are used); 0.3567 and 0.6667 are the mg amounts of potassium iodate and oxygen equivalent to 16 ml of a precisely 0.01 n solution of sodium thiosulfate (when a 0.05 n solution is used, these figures are replaced by 1.784 and 0.3334; for a 0.1 n solution, by 3.567 and 0.6667)*; V is the volume of the water being analyzed taken for the determination, with consideration of all previous dilutions (in ml).

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* The calculation of all these figures is based on the fact that in iodometric titration a gram-equivalent of potassium iodate is 1/6 of a gram molecule; according to the reaction equation given above, 5 atoms of oxygen correspond to 2 molecules of potassium iodate.

## APPENDIX 4. DETERMINATION OF THE SILVER CONTENT IN WATER (Kul'skiy, 1963)

The method is based on the extraction of silver from acid media by solutions of dithizone in organic solvents. As a result of the interaction between silver and dithizone, silver dithizonate is formed. Silver is extracted quantitatively from solutions containing chlorides with pH in the presence of trylon B, which binds metals that disturb the determination. In the pH change interval from 3.5 to 5 in the presence of trylon B, mercury and divalent platinum are readily extracted, as well as silver. These metals are not found in drinking water and so their influence is excluded in the determination of silver.

Solutions used. 1. Dithizone solution.

2. Acetic acid (dilution 1:4).

3. 10% solution of sodium acetate.

4. 0.01 n solution of trylon B, prepared by dissolving 1.68 g of the preparation in one liter of distilled water in a measuring flask.

5. A standard solution of silver nitrate is prepared by dissolving 1.577 grams of chemically pure $AgNO_3$ of distilled water in a 1 liter measuring flask; one ml of this solution contains 1 mg of $Ag^+$ ions. When it is diluted 100 times, a working solution is obtained, 1 ml of which contains 0.01 mg of $Ag^+$ ions.

6. A 1% solution of hydroxylamine sulfate or chemically pure urea.

Method of determination. For analysis, a sample is taken which contains 0.001-0.010 mg of silver. To this we add 0.01 n solution of trylon B with an approximately 10-fold excess in comparison with the required amount for binding the disturbing cations (1-5 ml), after which the pH of the solution is brought to 5 by adding 4 ml of acetic acid (dilution 1:4) and 20 ml of a 10% /246
sodium acetate solution. If the volume of the resultant solution is less than 50 ml, distilled water is added, then 5-10 mg of urea or 2 ml of a 10% solution of hydroxylamine sulfate, extracting in a separatory funnel; after allowing the solution to stand for 5 to 7 minutes, titration is carried out using a dithizone solution. For this purpose the dithizone solution in $CCl_4$ is added in batches of 0.3-0.5 ml and the silver is extracted, basically extracting the solution in a separatory funnel (1-2 minutes) with each batch of dithizone until the last batch fails to change its initial green color. (Separate extracts may not be added, but dithizone may be added until an intermediate greenish color of the extract is obtained). In a second separatory funnel, a sample is prepared for comparison, with the same chloride content as the solution under study; pH ~ 5. Then the same amount of dithizone solution is added to the test tube for comparison which was used to extract

the silver in the sample under test, then titrated with a standard solution of silver salt until the color of the extracts in both funnels is the same. The amount of standard solution of silver salt extracted during titration gives the amount of silver in the sample. The determination can also involve photocolorimetry. A change in the chloride content of the water by 30-40 mg/liter requires checking the calibration curve.

## APPENDIX 5. DETERMINATION OF ALUMINUM
(Lur'ye, Nikolayeva, 1953)

The method is based on the fact that aluminum oxyquinolate is quantitatively extracted with chloroform in a slightly acid medium (pH = 4.35-4.5), staining the chloroform layer a greenish-yellow color. On the basis of the intensity of this coloration, the aluminum content can be determined by colorimetric titration or the standard scale method. The iron which disturbs the determination can be oxidized beforehand to trivalent and extracted with chloroform in a more acid medium (pH = 1.8-2.0).

Reagents. Sulfuric acid, 1 n solution. Oxyquinoline, 2% solution in chloroform.

Acetate buffer solution, with 102 ml of a 1 M solution of acetic acid being mixed with 9 ml of a 1 M solution of sodium acetate to prepare it; then water is added up to 1 liter. The pH of the solution is 4.5.

Standard solution of aluminum salts. 1.759 g of aluminum alum (analytically pure) is dissolved in distilled water, then diluted up to 1 liter; 1 ml of the resultant solution contains 0.1 mg of aluminum. In determining very small amounts of aluminum, a 10-fold more dilute solution is used, 1 ml of which contains 0.01 mg of aluminum.

Method of determination. The volume of water to be analyzed is chosen so that it will contain 5-200 micrograms of aluminum; if distilled water must be added up to 25-50 ml, a small amount (on the point of a knife blade) of ammonium persulfate is added and stirred until it dissolves; the solution is allowed to stand several minutes and then transferred to a separatory funnel fitted with a ground glass stopper and neutralized with a 0.1 n solution of acid or alkali.

The amount of acid or alkali required for neutralization is found by titrating an individual batch of water to be analyzed against methyl orange. Then the solution is acidified by adding 1 n sulfuric acid at the rate of 0.4 ml per 25 ml of solution (after acidification, the pH of the solution will be 1.7-1.95). 1.5-2 ml of a 2% solution of oxyquinoline in chloroform is added, shaken vigorously, then allowed to stand until the layers separate out and the iron in the bottom layer, colored by the oxyquinolate, is decanted.

Extraction of iron from the solution is repeated once again by adding a similar batch of solution of oxyquinoline to the chloroform. When the iron content is less than 8 mg/liter, as is usually the case, very pale layers of chloroform are obtained in the second extraction; in this case, two extractions may suffice. When the iron content is high, extraction continues, adding new batches of chloroform solution until a colorless extract is obtained. /247

In the case of a solution that does not contain iron, 2.5-3.0 ml of a 2% solution of oxyquinoline in chloroform is added, together with 10 ml of

acetate buffer solution (pH = 4.5); then by shaking vigorously, the aluminum oxyquinolate is extracted. With the above-mentioned aluminum content, practically total extraction is achieved in one step. The solution is allowed to stand 1 to 2 minutes for the layers to separate and then the lower, yellowish-green chloroform layer is decanted into a test tube for colorimetric titration (about 25 ml of the water layer may be decanted as well). In another similar test tube, 15 ml of distilled water, 10 ml of the above-mentioned acetate buffer solution and as much oxyquinoline solution in chloroform as was added to the first solution are mixed. The fluid is titrated from a microburette with a standard solution of aluminum alum, 1 ml of which contains 0.1 mg of aluminum, with violent agitation of the test tube until the intensities of the colors in the two test tubes are the same.

With a very low aluminum content, titration is carried out with an alum solution diluted 10-fold, i.e., containing 0.01 mg of aluminum per ml.

Calculation. The aluminum content (x, in mg/liter) is calculated by the formula:

$$X = \frac{0.1 \cdot a \cdot 1,000}{V},$$

where a is the volume of a standard solution of aluminum salt used for titration until the colors are the same (in ml); V is the volume of waste water used for analysis (in ml).

Instead of the colorimetric titration, the method of comparison using the standard scale can be employed.[1]

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[1]The preliminary extraction of iron can be eliminated if the aluminum is extracted in an alkaline medium (pH = 8.35-11.0). The iron is then bound into a complex with sodium cyanide or potassium cyanide, while the magnesium is bound with Komplexon III.

APPENDIX 6.*| BRIEF DESCRIPTION OF CERTAIN SOVIET AND FOREIGN IONITES (Bogatyrev, 1968)



| Brand | Basis of Matrices | SEC (Static Exchange Capacitance), mg-eq/g: Soviet brands: On the basis of 0.1 N solution of $CaCl_2$ | SEC (Static Exchange Capacitance), mg-eq/g: Soviet brands: On the basis of 0.1 N solution of NaOH | SEC (Static Exchange Capacitance), mg-eq/g: Foreign brands | Maximum working temperature, °C | Country of Manufacture |
|---|---|---|---|---|---|---|
| **Cationites** | | | | | | |
| KU-2 | Styrene, divinylbenzene | 4,3—4,9 | 4,9—5,1 | — | 120—130 | USSR |
| SDV | | 4,0 | 4,2 | — | — | USSR |
| Amberlite, IR-120 | | — | — | 4,58 | 120 | USA |
| Amberlite, IR-200 | | — | — | 5,0 | 120 | USA |
| Dowex-50 | | — | — | 4,8 | 150 | USA |
| Duolite S-20 | | — | — | 4,9 | 100 | USA |
| Levatite S-100 | | — | — | 4,75 | 100 | FRG |
| Ionenaustauscher-1 | Styrene | — | — | 4,5 | 110 | FRG |
| Amberlite KhYe-100 (IR-112) | | — | — | 4,5 | 120 | USA |
| Chempro S-80 S-25 | | — | — | 4,3—4,7 | — | USA |
| Ionak S-240 | | — | — | 4,9 | 120 | USA |
| Katex S | | — | — | 4,9—5,0 | 120 | Czechoslovakia |
| Mukion RS, PSM | | — | — | 4,0 | — | Hungary |
| Nal'tsit HCR | | — | — | 4,5 | — | Great Britain |
| Permutite Q-225 | | — | — | 4,3 | 120 | USA |
| Permutite RS | | — | — | 5,2 | — | FRG |
| Vofatite KPS-200 | | — | — | 4,5 | 115 | GDR |
| Zeokarb-225 | | — | — | 4,9 | 100 | Great Britain |
| SBS | Styrene, Butadiene | 2,3—2,7 | 2,8—3,0 | — | — | USSR |
| KU-21 | Naphthaline-Sulfonic acid, formaldehyde | 4,5 | 5,5 | — | — | USSR |
| KU-1 | Phenol, formaldehyde | 1,8—2,25 | 4,5—5,1 | — | 90 | USSR |
| Amberlite IR-100 | | — | — | 1,75 | — | USA |
| Amberlite IR-105G | | — | — | 2,7 | — | USA |

*Note: Commas indicate decimal points.

| Brand | Basis of Matrices | SEC (Static Exchange Capacitance), mg-eq/g | | | Maximum working temperature, °C | Country of Manufacture |
|---|---|---|---|---|---|---|
| | | Soviet brands | | Foreign brands | | |
| | | On the basis of 0.1 N solution of $CaCl_2$ | On the basis of 0.1 N solution of NaOH | | | |
| Dorolite-KF | | — | — | 2,7 | — | Hungary |
| Mukionite FG | | — | — | 2,8 | — | Hungary |
| Vofatite F | | — | — | 2,5 | 30—50 | GDR |
| MSF-3 | Chlorobenzosulfonic acid, formaldehyde | 1,8 | 4,3 | — | — | USSR |
| Amberlite IR-105 | Phenol, formaldehyde | — | — | 2,7 | — | USA |
| Dowex-30 | | — | — | 4,3 | — | USA |
| Duolite C-1, C-3 | | — | — | 3,2 | 80 | USA |
| Levatite-PN | | — | — | 2,25 | 95 | FRG |
| Mukion-P | | — | — | 2,2 | — | Hungary |
| Nal'tsit-MX | | — | — | 3,0 | — | USA |
| Vofatite-P | | — | — | 1,9 | 97 | GDR |
| Zeokarb-215 | | — | — | 2,6 | 40 | Great Britain |
| Zeokarb-315 | | — | — | 2,2 | 95 | Great Britain |
| Zerolite-215 | | — | — | 2,6 | 30 | Great Britain |
| Zerolite-315 | | — | — | 2,6 | 95 | Great Britain |
| KM | Methacrylic acid | 0 | 7,4—7,6 | — | — | USSR |
| KMT | | 0,4 | 10,1 | — | — | USSR |
| SG-1 | | | 8,9 | — | — | USSR |
| Amberlite IRS-50 | | — | — | 10,0 | 125 | USA |
| Duolite CS-101 | | — | — | — | 80 | USA |
| Ionak C-240 | | — | — | 8,2 | 40 | USA |
| Ionenaustauscher-IV | | — | — | 10,0 | 110 | FRG |
| Muckion-CP | | — | — | 8,0 | — | Hungary |
| Permutite-226 | | — | — | 5,3 | — | Great Britain |
| Permutite H-70 | | — | — | 8,2 | — | USA |
| Permutite C | | — | — | 9,0 | 80 | FRG |
| Zeokarb-226 | | — | — | 9,0 | 100 | Great Britain |
| KB-4 | Methyl ether of methacrylic acid, divinylbenzene | 0,1 | 8,5—9,5 | — | 150—180 | USSR |
| KF-1 | Styrene, divinylbenzene | 0,5 | 5,0 | — | — | USSR |
| Duolite C-61 | | — | — | 7,4 | 80 | USA |
| Nal'tsit KH-219 | | — | — | 8,8 | — | USA |
| KF-3 | Vinylnaphthaline, divinylbenzene | 0,5 | 3,5 | — | — | USSR |
| RF | Mono- and diresorcinophosphate | — | 5,0 | — | | USSR |

*Note: Commas indicate decimal points.

| Brand | Basis of Matrices | SEC (Static Exchange Capacitance), mg-eq/g | | | Maximum working temperature, °C | Country of Manufacture |
|---|---|---|---|---|---|---|
| | | Soviet brands | | Foreign brands | | |
| | | On the basis of 0.1 N solution of $CaCl_2$ | On the basis of 0.1 N solution of NaOH | | | |
| AV-17 | Styrene, divinylbenzene | 3,5—4,0 | 4,8 | — | 60 | USSR |
| Amberlite IRA-400 | | — | — | 2,5—3,9 | 50 | USA |
| Amberlite IRA-401 | | — | — | 3,0—4,0 | 50 | USA |
| Amberlite IRA-410 | | — | — | 3,9 | 40 | USA |
| Amberlite IRA-411 | | — | — | 3,0 | 40 | USA |
| Anex S-8-TM | | — | — | 3,7—3,9 | 40 | Czechoslovakia |
| Dowex-1 | | — | — | 2,5—3,5 | 50 | USA |
| Dowex -2 | | — | — | 2,5—3,6 | 30 | USA |
| Dowex 21-K | | — | — | 4,5 | 50 | USA |
| Duolite A-40, A-42 | | — | — | — | — | USA |
| Ionenaustauscher-III | | — | — | — | 40 | FRG |
| Permutite ES | | — | — | 5,0 | 40 | USA |
| Permutite S-2 | | — | — | 3,3—3,7 | — | USA |
| Zeolite FF | | — | — | 3,5 | 60 | Great Britain |
| ASD-2 | Styrene, Trimethyldiamine | — | 1,34 | — | — | USSR |
| EDE-10P | Polyethylene Polyamines, epichlorhydrin | — | 9,0—9,5 | — | 60 | USSR |
| Levatite M-1 | | — | — | 10,2 | 40 | FRG |
| PEK | | 1,88 | 6,0 | — | — | USSR |
| Anex OAL | Pyridine, aliphatic amines | — | — | — | — | Czechoslovakia |
| Ionak A-243, A-3000 | Polyethylene polyamines, urea, guanidine | — | — | 7,4 | 45 | USA |
| Amberlite IR-4B | Polyethylene-polyamines, phenol, formaldehyde | — | — | 9,2 | 40 | USA |
| AN-19 | Styrene, Divinylbenzene | — | 6,0 | — | — | USSR |
| Anex PA | Aromatic amines, formaldehyde | — | — | 8,0 | 50 | Czechoslovakia |
| Deacidite E | Phenol, aliphatic amines, formaldehyde | — | — | 7,0 | — | GDR |

*Note: Commas indicate decimal points.

| Brand | Basis of Matrices | SEC (Static Exchange Capacitance), mg-eq/g | | | Maximum working temperature, °C | Country of Manufacture |
|---|---|---|---|---|---|---|
| | | Soviet brands | | Foreign brands | | |
| | | On the basis of 0.1 N solution of $CaCl_2$ | On the basis of 0.1 N solution of NaOH | | | |
| Dowex-3 | Polystyrene | — | — | 5,5—6,0 | 65 | USA |
| Duolite A-1, A-2 | Phenol, polyethylene, polyamines | — | — | 5,4—7,0 | 35 | USA |
| Levatite M | Aminophenol, formaldehyde | — | — | 3,5 | — | FRG |
| Vofatite M | Phenolene diamine, formaldehyde | — | — | 7,0 | 30 | GDR |
| Av-18 | Styrene, divinylbenzene, pyridine | 1,5 | 3,0 | — | — | USSR |
| Av-16 | Polyethylene polyamines, pyridine, epichlorhydrin | — | 9,8—10,5 | — | — | USSR |
| An-1 | Melamine, formaldehyde | — | 4,0—4,5 | — | 30 | USSR |
| An-2F | Polyethylene polyamines, phenol | — | 9,—10,5 | — | 40 | USSR |
| Ionak 293-M | | — | — | 6,0 | — | USA |
| Permutite E | | — | — | 9,0 | 80 | USA |

*Note: Commas indicate decimal points./

APPENDIX 7. PREPARED MIXTURES OF IONITES PRODUCED FOR WATER PURIFICATION PROCESSES (Osborn, 1964)

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| Name | Composition, Form | Working Temp., Max. °C | Note |
|---|---|---|---|
| Monobed MB-1 | Amberlite IR-120 | 60 | Eliminates all ions (anions $CO_3^{2-}$, $HSiO_3^{2-}$ and other weak acids) |
| Monobed MB-2 | Amberlite IR-120 (H) | 40 | Analogous to MB-1, but has larger capacity. |
| | Amberlite IRA-A-410 (OH) | -- | --- |
| | Amberlite IR-120 (H) | 40 | Similar to MB-2 but contains dye which indicates the limit of saturation. |
| Monobed MB-4 | Amberlite IR-120 (H) | 60 | --- |
| | Amberlite IR-45 (OH) | -- | --- |
| Monobed MB-5 | Amberlite IRC-50 (H) | 40 | --- |
| | Amberlite IRA-410 (OH) | -- | --- |
| Monobed MB-6 | Amberlite IRC-50 (H) | 60 | --- |
| | Amberlite IR-45 (OH) | -- | --- |
| Bio-deminrolite | Zeokarb-225 (H) | 60 | Eliminates all ions (anions $CO_3^{2-}$, $HSiO_3^{2-}$ and other very weak acids) |
| | Deacidite FF (OH) | -- | |
| Indicator bio-deminrolite | Zeokarb-225 (H) | 60 | Similar to bio-deminorolite but contains a dye that indicates the saturation limit. |
| Amberlite XE-149 (Monobed)* | Amberlite XE-151(K) | -- | Filtrate -- dilute solution of KOH. |
| | Amberlite XE-78(OH) | | |
| Amberlite XE-150 (Monobed) | Amberlite XE-77(H) | -- | --- |
| | Amberlite XE-78(OH) | -- | --- |
| Amberlite XE-154 (Monobed)* | Amberlite XE-163 | -- | Filtrate -- dilute solution of KOH. |
| | Amberlite XE-78(OH) | | |
| | Amberlite XE-163($NH_4$) | -- | Filtrate -- dilute solution of LiOH. |
| | Amberlite XE-78(OH) | -- | |
| | Amberlite XE-169(OH) | -- | Filtrate -- dilute solution of $NH_4OH$ |
| Amberlite E-170 (Monobed)* | Amberlite XE-78(OH) | | |

*Mixtures for purification of water used in nuclear reactors.

APPENDIX 8. FRACTIONAL COMPOSITION OF SEVERAL IONITES
(Shkrob, Prokhorov, 1961)

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| Cationite | Country of mfg. | Fractional content, % | | | | | |
|---|---|---|---|---|---|---|---|
| | | 0.3 mm | 0.3-0.4 mm | 0.5-0.75 mm | 0.75-1 mm | 1.0-1.5 mm | 1.5 mm |
| KU-1 | USSR | 2.4 | 15.0 | 25.8 | 24.3 | 15.0 | 17.5 |
| KU-2 | USSR | 5.0 | 50.0 | 40.0 | 4.0 | 1.0 | 0.0 |
| KU-1G | USSR | 2.0 | 10.0 | 23.0 | 61.0 | 4.0 | 0.0 |
| Vofatite R | GDR | 14.0 | 38.5 | 38.9 | 4.0 | 3.2 | 1.4 |
| Zeokarb | USA | 2.0 | 28.3 | 31.0 | 29.0 | 7.8 | 2.2 |
| Amberlite IR-100 | USA | 2.4 | 31.8 | 40.2 | 21.2 | 2.2 | 2.2 |
| C-50-A | France | 4.0 | 43.5 | 37.5 | 15.0 | 0.0 | 0.0 |
| Allassion | France | 16.1 | 32.8 | 31.4 | 17.0 | 2.7 | 0.0 |

| Anionite | Country of mfg. | Fractional content, % | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 1.6 mm | 1.6-0.85 mm | 0.85-0.6 mm | 0.6-0.42 mm | 0.42-0.31 mm | 0.31-0.2 mm | 0.20 mm |
| **Strongly Basic** | | | | | | | | |
| EDE-10P | USSR | 18.0 | 30.5 | 11.0 | 39.2 | 0.4 | 0.6 | 0.3 |
| AV-16 (AM) | USSR | 2.0 | 25.0 | 32.0 | 29.0 | 6.0 | 5.0 | 1.0 |
| AV-17 (AMP) | USSR | -- | 1.7 | 21.7 | 35.2 | 24.5 | 14.8 | 2.1 |
| AV-27 | USSR | -- | 19.0 | 53.0 | 22.0 | 5.0 | 1.0 | -- |
| Amberlite IRA-400 | USA | -- | 0.75 | 38.8 | 37.3 | 16.4 | 6.0 | 0.75 |
| IRA-401 | USA | -- | -- | 7.7 | 56.5 | 21.8 | 12.8 | 1.2 |
| IRA-410 | USA | -- | 1.4 | 25.0 | 47.3 | 19.4 | 5.5 | 1.4 |
| Levatit MN | FRG | -- | 36.25 | 31.25 | 7.5 | 15.0 | 8.75 | 1.25 |
| Allassion AQ-17 | France | -- | 8.0 | 43.0 | 38.0 | 10.0 | 1.0 | -- |
| Dianon SA-100 | Japan | -- | -- | 0.9 | 42.0 | 42.0 | 14.2 | 0.9 |
| **Weakly Basic** | | | | | | | | |
| AN-2Fg | USSR | 1.3 | 31.7 | 20.8 | 19.2 | 21.6 | 5.4 | 0.0 |
| AN-18 | USSR | 0.0 | 9.0 | 39.0 | 32.0 | 13.0 | 5.0 | 2.0 |
| AN-1 | USSR | 1.0 | 51.0 | 30.0 | 11.0 | 5.0 | 2.0 | 0.0 |
| Amberlite IR-4B | USA | 0.0 | 0.0 | 14.2 | 54.3 | 29.0 | 2.5 | 0.0 |
| Vofatite L-150 | GDR | 0.0 | 58.0 | 23.0 | 12.0 | 4.0 | 2.0 | 1.0 |

## APPENDIX 10. DETERMINATION OF MECHANICAL STRENGTH*

Solutions, vessels and instruments used:

- distilled water, AUSS** 6709-53;
- graduated cylinder, AUSS** 1770-64, capacity 50 ml;
- set of sieves with grids according to AUSS** 3584-53;
- instrument for determining the mechanical strength (type PMPI-46 or rype MII-62) designed by the Scientific Plastics Research Institute.

Tests performed. The working fraction of cationite is placed in the graduated cylinder (50 ml capacity) and compacted by pounding the bottom of the cylinder on a wooden surface.

About 50 ml of the compacted cationite, plus distilled water measured with an accuracy up to 1 ml, was placed in a two-cone vessel of a type PMPI-46 instrument or an MII-62 instrument to determine the mechanical strength. The two-cone vessel was previously calibrated with water to the 70 ml mark.

The excess water was decanted up to the measuring mark, the vessel was clamped in a flask holder and the test was performed under the following conditions:

- frequency of vibrations of the handle of the flask holder - 135 lifts per minute;
- height of lift of the handle -- 220-225 mm.

After two hours of operation of the device, the contents of the two-cone vessel were transferred to a screen whose grid number corresponded to the lower limit of fractional composition of the cationite under test. After sowing in distilled water by means of a graduated cylinder, the volume of the cationite that remained on the grid was measured with an accuracy up to 1 ml (following compaction).

The mechanical strength of the cationite ($\sigma_m$) in percent is calculated by the formula

$$\sigma_m = \frac{V_1 \cdot 100}{V},$$

where V is the volume of cationite used for the test (in ml) and $V_1$ is the volume of cationite left in the sieve (in ml).

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*All-Union State Standard 13505-68, Moscow, Standards Press, 1968.
**AUSS = All-Union State Standard.

## APPENDIX 9. DETERMINATION OF THE FRACTIONAL COMPOSITION*

The fractional composition and the content of the working fraction are determined according to All-Union State Standard 10900-64 (Section B). Swelling of cationites takes place in distilled water (AUSS 6709-53) in one hour. /254

Sowing of cationites is accomplished in distilled water, while the sowing of cationite brand KU-1G is accomplished with the addition of 5 ml of 0.01% solution of auxiliary substance OP-7 or OP-10 (AUSS 8433-57) to prevent its floating.

The working fraction was assumed to be the residue between sieves with AUSS 3584-53 screens whose number corresponds to the upper and lower limits of the fractional composition of the cationite under test.

*All-Union State State Standard 13505-68, Moscow, Standards Press, 1968.

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